Application No. 09/894,375
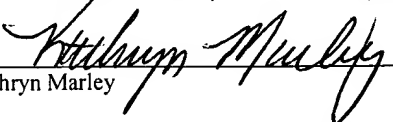
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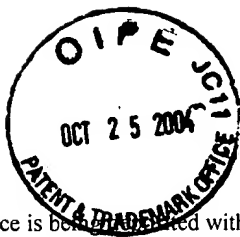
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of inventor(s):

Leonard Nanis

Application No. **09/894,375**

Confirmation No. **5531**

Filing Date: **27 June 2001**

Title: **Method of Coating Smooth Electroless Nickel on Magnetic Memory Disks and Related Memory Devices**

Group Art Unit: 1753
Examiner: Rodney G. McDonald

CUSTOMER NO. 22470

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Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION OF INVENTOR UNDER 37 CFR §1.132

1. I, Leonard Nanis, am inventor of the invention claimed in the application identified above. In addition, I am an expert in disk drive manufacturing, particularly as it relates to materials science and electrochemistry. Attached hereto as Exhibit A is a copy of my resume.

2. This Declaration sets forth background information concerning the microstructural variations that result from the surface polishing of metal substrates, which we have characterized as cold-working which results from polishing, and addresses the prior art analyzed by the Examiner in the present application.

3. To avoid misunderstanding, surface roughness is NOT the same as "cold-worked surface". The cold working in polished metals results from the mechanical abrasion caused by the polishing slurry. It is well known that polishing results in a layer of material in which residual stress from the polishing alters the mechanical structure of the material. The present

invention does not mask surface roughness, and indeed carries the original roughness through the plating. Rather it masks microstructural variations caused by the cold-working during polishing that would otherwise cause the plating to be non-uniform and cause the carpeting effect.

4.   A few words about polishing are appropriate. On a micro-scale, polishing is not a gentle procedure. Polishing is always accompanied by pressure on the surface which pushes abrasive particles, suspended in a slurry, into the metal surface and also moves the abrasive forward to cut through any protruding surface features. The abrasive particles are also crushed and broken to reveal fresh sharp cutting edges. It is the pressure of the polishing pad on an abrasive particle touching the surface that produces a highly localized stress pattern within the metal, just beneath the surface point of contact. As metal is cut, it is also plowed to the sides of the cut, there to be further cut and/or burnished flat by the next passing abrasive particles.

5.   All of the randomized chaotic micro-scale cutting and distortion beneath the metal surface is classed as cold-working. The result is a shiny surface.

6.   The important aspect is that the cold-worked metal beneath the shiny surface is non-uniformly distorted. Any subsequent chemical treatment, such as etching to remove oxide in preparation for plating, will be non-uniform, influenced by the chaotic pattern of the atomic structure stored in the distorted sub-surface region.

7.   The sub-surface region has been known for 100 years as the Beilby layers and is believed to also include particles of the naturally formed metal oxide as well as embedded fine abrasive particles. Exhibit B attached hereto is an excerpt from Bhushan, INTRODUCTION TO TRIBOLOGY, John Wiley and Sons (2002), pages 9-11. The Beilby layers and cold-worked layers are clearly described, and distinguished from surface roughness by Bhushan.

8.   The Examiner's attention is drawn, for example, to Okano et al. US 5,221,459 (Exhibit C). Okano et al. describes a cold-worked layer that extends 20 Angstroms or more beneath the surface of mirror-polished titanium. Okano et al. teaches that a titanium substrate includes structural defects that result from polishing, which should be removed by etching before

anodizing the titanium. It is the layer of structural defects at the surface due to this strain from polishing which is referred to as the cold worked surface in the present application.

9.   Okano et al. was embarked in 1992 in an effort to use titanium as a memory disk substrate. Along the way, Okano et al. overcame problems caused by a cold-worked layer due to polishing.

10.   To review briefly, Okano et al. began by adding a hard layer of titanium oxide on smooth, mirror-polished titanium. The titanium oxide was grown by the wet electrochemical process of anodizing, similar to the well-known anodizing of aluminum.

12.   Magnetic memory layers were then sputtered onto said anodized surface. At first, when tested, the magnetic performance was disappointing because of too many missing pulses--places where the magnetic layer was essentially missing.

13.   With further study, Okano et al. determined that the problem of missing pulses was due to (column 2, line 39) "non-uniformity of the anodized film." The inventors overcame the problem by finding that (column 2, line 44) "...a uniform anodized film can be made if the titanium substrate is chemically etched, removing its surface portion of a specified thickness."

14.   Okano et al. explains the good results obtained by etching before anodization in column 2, lines 49-61 as: "When it is mirror-polished, its surface portion will be altered by the mechanical process and will have strain or defects. An anodized film, if formed on the surface of the substrate, thus altered, is non-uniform and has defects."

15.   Okano et al. has nicely described cold-worked Beilby layers and, from etching parameters, provides a quantitative measure of its depth beneath the surface as ranging from 20 to 2000 Angstroms.

16.   Let me supplement Okano with a few lines about cold-worked sub-surface layers from the Metals Handbook, Volume 8 of the 8th edition (Exhibit D). The chapter entitled "Principles

of Technique Selection in Mechanical Polishing" (pages 14-26) offers practical advice for polishing metal specimens for microscopy and frequently notes that polishing produces a distorted layer that must be removed (etched) in order to reveal the true structure of the metal. For example, a section titled "Polishing Damage" includes the statements: "...mechanical polishing always produces a series of scratch grooves on the surface of the specimen" (page 19)

"...a plastically deformed damaged layer is also introduced" (page 19)

"The presence of a damaged layer cannot be avoided by the use of polishing in which the abrasive, no matter how fine, is suspended in a liquid..." (page 20)

"It is a frequent annoyance in metallographic practice to find that a surface that appeared to be free of scratches...turns out to be severely scratched after etching" (page 21)

"Scratches are attacked preferentially during etching because of the disturbed metal, or damaged layer, associated with them." (page 21)

17.   Okano et al. and skilled metallurgists know there is a damaged layer due to polishing. Platers know that surface oxides have to be etched off to assure good bonding between the plated layer and the substrate. Metallurgists also know that etching of the damaged layer is non-uniform. So here is a Catch-22 situation---we have to etch to plate, but etching will non-uniformly roughen the otherwise smooth polished surface.

18.   The present invention is based on the discovery that these microstructural variations are masked by the claimed process. The Examiner attempts to construct motivation for a combination of Suenaga (US 5,478,657) and Nanis (US 5,405,646) (hereinafter Nanis I) as prior art for this Application.

19.   The prior art establishes two facts:
        (1) Nanis I taught a process like that claimed herein, as applied for masking chemical variations caused by impurity inclusions in the metal surface; and
        (2) Super smooth titanium substrates existed and are hard to plate with NiP.

20.   These conclusions do not connect Suenaga and Nanis I, and at most suggest it might be "obvious to try" Nanis I on a super smooth substrate. The prior art establishes that plating super

smooth metal with NiP is problematic. On aluminum, carpeting occurs. Suenaga finds that you can plate NiP on super smooth titanium only in a narrow set of conditions, and only with marginal results. The present invention, however, provides that metal substrates can be successfully plated with NiP, even if they include Beilby layers, by following the Nanis I process. Nanis I however does not mention super smooth substrates.

21.   We don't doubt that Beilby layers occur with Suenaga's mirror-polished titanium surface including microstructural variations in the metal. Since Suenaga was a co-inventor on the Okano et al. patent described above, the layer was certainly known to Suenaga and probably influenced him to avoid conventional wet surface methods (etchants and oxidation preventers) commonly used to prepare titanium for N-P plating. See, Gawrilov, CHEMICAL (ELECTROLESS) NICKEL PLATING, Portcullis Press Ltd. (1979), pages118-119, attached as Exhibit E.

22.   In terms of prior art, there is absolutely NOTHING stated in Suenaga about a "cold-worked surface" that could serve as even a hint for our invention.

23.   We are concerned only with getting a polished surface with its hidden sub-surface distorted metal to be DRY vacuum seeded in preparation for WET electroless NiP deposition. By avoiding non-uniform etching in the WET surface preparation for WET NiP plating, we have demonstrated a way to preserve the initial smooth surface finish of a pre-polished substrate, thus simplifying the later polishing of the plated NiP layer. As an example, our invention avoids the problem of "carpet" patterns on conventionally etched and zincated polished aluminum. We also recognize the generality of the problem for all polished metals that are possible substrates for memory disks and we provide the solution to the problem.

24.   The unexpected results achieved by the present invention as illustrated with reference to Exhibits F, G and H. Exhibit F includes copies of photographs provided by OMG-Fidelity of a supersmooth aluminum substrate after etch (2nd Zincate) and after plating with NiP, using a "standard process" and a so-called "advanced process" developed by OMG-Fidelity, of Newark, New Jersey. The "advance process" was represented to me as being based on a modification of

the wet zincate chemistry used to etch the super finished aluminum prior to plating, and to add zinc to screen the aluminum from oxidation.

25.   The starting substrate for the OMG-Fidelity process was "super finished aluminum". If plated conventionally, a rough surface as a result of "carpeting" is obtained as shown for the "Standard Process" as shown in the two optical photos at about 900X on the left column of the Exhibit. As shown in the right column of the Exhibit, some improvement was obtained by OMG-Fidelity, using the Advanced Process. However, super finished aluminum plated with the process of the present claims, was compared with the results of the best surface achieved by OMG-Fidelity using the "Advanced Process" using scanning electron microscopy SEM. No surface features were visible even at higher magnification (1500X) for the claimed invention, while some texture was still visible on the "advanced process" surface under the SEM as shown in Exhibit G. In fact, an SEM photo of the results of the claimed process is featureless, because it is so smooth.

26.   Exhibit H is a SEM photo at 1500X of an aluminum substrate, plated according to the claimed invention, which was subjected to severe bending as an adhesion test. The photograph shows a crack at 1500X, in the same NiP plated Aluminum substrate mentioned in the present application, and prepared as described in paragraphs [0055] and [0056] of the application. The crack was created by severe bending of the disk to test adherence of the NiP layer. No exfoliation is seen in the photo, evidencing excellent adhesion.

27.   The NiP layer is intact on either side of the crack, shown in the middle of the photograph, where the crack extends into the aluminum substrate. The super smooth surface of the NiP layer is evident in the areas of the surface that are not affected by the cracking. In fact, the smoothness is dramatic, compared to the OMG-Fidelity "Advanced Process" plating shown in Exhibit G.

28.   Included on the page with the EXHIBIT H attached hereto, is 1500X SEM photograph of a control disk, plated with the conventional double zincate plating process, also mentioned in the application in paragraphs [0055] and [0056]. The edge of the crack in the control disk is on the lower edge of the photograph. The surface of the control disk shows significant "carpeting."

The smoothness of the disk plated according to the present invention is dramatic compared to the control disk. Proof of dramatic, unexpected results by practice of the present invention is therefore established.

29.   Suenaga attempted, as far as can be determined from the specification, to use NO treatment after polishing. Far from suggesting that Nanis I should be utilized to address the problem of masking the microstructural variations in the surface of a super smooth metal, Suenaga suggests directly plating NiP on the untreated, polished metal. Suenaga's results are mixed, at best, with adhesion rates that would not support commercial use. But, Suenaga does not lead to application of the Nanis I process.

30.   Suenaga does not use the 15-20 micron conventional layer thickness for NiP on aluminum because a layer thicker than 5 microns will break loose (exfoliate) from titanium when heated later in magnetic sputtering (Suenaga, column 3, lines 1-6 and column 4, lines 56-63).

31.   At the same time, Suenaga has to plate more than the lower limit of 0.09 micron NiP in order to have enough for texturing without cutting through to titanium, column 3, lines 15-17 and column 4, lines 44-46. Thus, in a trade-off between exfoliation and texturing, Suenaga MUST use a thinner than usual NiP layer that is less than 5 microns thick but greater than 0.09 micron. It is not as if, as the Examiner asserts, Suenaga has accomplished a goal of thinner NiP by using polished titanium with Ra = 20 Angstrom. Suenaga's thinner NiP actually reflects a problem with the use of smooth titanium, that is poor adhesion which results in exfoliation. This fact makes the Suenaga idea practically unusable in a commercial setting, leading to a conclusion that super smooth titanium substrate would be very difficult to use in practice.

32.   Suenaga tells us nothing about the numerical value of surface roughness of the plated NiP. Instead, in column 6, lines 10-11, Suenaga settles for what he gets when plating NiP in the exfoliation-free range of 0.09 to 5 microns PROVIDED the polished titanium has an initial surface roughness between 0.0002 and 0.006 micron (2-60 Angstroms). Suenaga provides no numerical roughness data to support a claim of an improved surface roughness of the medium.

33.   In column 3, line 66 to column 4, line 2, Suenaga teaches that "A plated layer on the titanium disc by the present invention is too thin to even out the surface roughness of the titanium disc Thus, Ra of the titanium disc itself should be at a level suitable for a magnetic disc."

34.   There are NO mention of an improvement of surface roughness and no numerical comparisons to assess. We should recall that Suenaga wants to AVOID POLISHING plated NiP and thus settles for Ra = 0.0060 micron (60 Angstroms) AFTER texturing the plated NiP. We find NO numerical information in Suenaga for roughness after plating but before texturing, other than general yes-no symbols in Table 1.

35.   At the time of my invention which resulted in Nanis I, no polishing was being done on substrates before plating NiP. The plating problems found with conventional surface activation of polished aluminum, the zincate "carpet" effect associated with a sub-surface distorted metal layer, came much later.

36.   It is true that both Nanis I and Suenaga use NiP. However, the question here is motivation to apply the process of Nanis I to a super smooth substrate, like the smooth substrate used by Suenaga. Suenaga teaches directly applying NiP plating on a smooth titanium substrate, and achieves results with poor adhesion, suggesting that the process is not commercially feasible. Nanis I teaches sputtering an intermediary layer on a substrate characterized by inclusions of impurities, to mask the chemical reactions with the impurities and improve the plating process. Nanis I does not address the problem of the Beilby layers at all. No one having skill in the art would be led to use a super smooth substrate as a starting point in the Nanis I process, based on the teaching of Suenaga.

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37.   I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Title 18, United States Code, '1001 and that such willful false statements may jeopardize the validity of any patent issuing from Application No. 09/894,375, and related cases.

Leonard Nanis

Leonard Nanis

19 October 2004

Date

Attachments: Exhibits A-H

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WORK EXPERIENCE

**CONSULTANT, MATERIALS SCIENCE AND ELECTROCHEMICAL
ENGINEERING
April 1989 to present (October 2004)**

OMG-FIDELITY:
    electrochemistry, electroplating.
MILLENNIUM MATERIALS:
    surface analysis, electroless plated high-strength memory disk material.
MMC TECHNOLOGY-MAXTOR:
    sputtering on glass memory disks.
TRUFOCUS:
    sputtered coatings for X-ray tube components.
DYTAK:
    developed composite electroplated nickel-silicon carbide wear-resistant
    contacts for membrane probes for wafer level evaluation of integrated
    circuit parameters, US 6,359,337.
QUANAM (BOSTON SCIENTIFIC):
    manufacture and electropolishing of stainless steel medical devices
    (angioplasty stents)
EMBOLIC PROTECTION (BOSTON SCIENTIFIC):
    manufacture of medical devices with nickel-titanium alloy (angioplasty).
RITA:
    manufacture of medical devices with nickel-titanium alloy (non-invasive
    radiofrequency tumor ablation).
HAMMON PLATING:
    scanning electron microscopy, plated gold, electroless nickel, sputtered
    transparent coatings on gold, established analytical laboratory for plating
    quality control.
LN3:
    developed thin film sputtered seed layers for electroless nickel plating on
    memory disk substrates, US 5,405,646.
APPLIED MATERIALS:
    electroless nickel, aluminum anodizing, corrosion.
ADVANCED CARDIOVASCULAR SYSTEMS (now GUIDANT):
    developed method for soldering titanium-nickel alloys, US 5,695,111;
    micromechanical medical devices, US 5,348,693.

VICE PRESIDENT, INFORMATION MEMORIES CORP.
February 1988 to April 1989

Responsible for production technology, advanced product development and corporate strategic planning, magnetic memory disks.

VICE PRESIDENT, DASTEK
January 1987 to September 1987

Reorganized and guided thin-film head technology and business strategy of merged Dastek and Datapoint (now Ahead Technology) to profitability; invented "waffle" contact burnish head for sputtered disks, US 4,845,816 .

SENIOR SCIENTIST, XEBEC
October 1984 to September 1987

Coordinated corporate materials science in all aspects of disk drives, including sputtered glass bonding of ferrite magnetic heads, printed circuit boards, head-disk lubricants, and heat treatment of substrates.

VICE PRESIDENT AND FOUNDER, SEAGATE MAGNETICS
September 1982 to January 1984

Demonstrated to Seagate that sputtered thin film media could be mass produced. As founder of Grenex, I met the challenge of outfitting a start-up, hiring and leading a technical team to produce finished thin film media within six months. As Director, made major contributions to strategy for successful second round financing and ultimate purchase of Grenex by Seagate Technology. Developed FACT accelerated corrosion test for memory disks.

MANAGER, ELECTROCHEMISTRY GROUP, SRI INTERNATIONAL
October 1975 to June 1982

Directed government and industry sponsored studies·of novel batteries, fuel cells, and extractive metallurgy for low-cost silicon for solar cells, US 4,584,181; US 4,748,014; US 5,110,531.

EDUCATION

Doctor of Engineering Science, Extractive Metallurgy, Columbia University
S.B., S.M., Metallurgy, Massachusettts Institute of Technology

PROFESSIONAL ACCOMPLISHMENTS

Consulting Professor, Materials Science, Stanford University

Professor, Chemical and Biochemical Engineering, Univ. of Pennsylvania
        1965 to 1975; Taught graduate and undergraduate courses in heat and
mass transfer, fluid mechanics, applied mathematics and electrochemical
engineering. Directed research on batteries, field ion microscopy, current
distribution in electrochemical systems and corrosion.

Organized Workshops on Materials Science in the Memory Storage Industry
        IIST, Santa Clara University, 1985;
        Stanford University, 1987

Chairman, Electrochemical Society, Industrial Electrolytics,1980 to 1982

Director and Founder, TruFocus Corp., Watsonville CA (X-ray tubes), 1988.

Invited Keynote Speaker, Hydrogen Embrittlement,
        Gordon Research Conference, New London, NH, 1980

Invited Keynote Speaker, Symposium for Environment-Sensitive Fracture of
Engineering
        Materials, Metallurgical Society, Chicago, 1977

Invited Keynote Speaker, Electrochemical Current Distribution, Gordon
Research Conference,
        Santa Barbara CA , 1974

Received A.S.T.M. Templin Award for studies of hydrogen in iron, 1970

PUBLICATIONS (partial list)

Double Zincate Treatment for Electroless Nickel Plating, Proceedings of Applied
Electrochemistry Conference, Hokkaido University, Japan, Aug 1994.

Analysis of Convective Mass Transfer by Potential Relaxation, J.
Electrochemical Society, v136 (1989) p1727.

Electrochemical and Environmental Corrosion Tests for Cobalt Alloy Disks,
IEEE Transactions v MAG21, 1985

Field Ion Microscopy, Chapter 9, Treatise of Electrochemistry, v8, White,
Bockris, editors, Plenum Publishing, NY, 1984

Chemical and Electrochemical Factors Affecting Hydrogen Absorption in Metals, Environment-Sensitive Fracture of Engineering Materials, Z.A. Foroulis, editor, Conference Proceedings, Metallurgical Society of A.I.M.E., 1979, p361

Chapter 2

SOLID SURFACE CHARACTERIZATION

2.1   THE NATURE OF SURFACES

A solid surface, or more exactly a solid–gas or solid–liquid interface, has a complex structure and complex properties dependent upon the nature of solids, the method of surface preparation, and the interaction between the surface and the environment. Properties of solid surfaces are crucial to surface interaction because surface properties affect real area of contact, friction, wear, and lubrication. In addition to tribological functions, surface properties are important in other applications, such as optical, electrical and thermal performance, painting, and appearance.

The solid surfaces, irrespective of the method of formation contain irregularities or deviations from the prescribed geometrical form (Thomas, 1982; Whitehouse, 1994; Bhushan, 1996). The surfaces contain irregularities of various orders ranging from shape deviations to irregularities of the order of interatomic distances. No machining method, however precise, can produce a molecularly flat surface on conventional materials. Even the smoothest surfaces, such as those obtained by cleavage of some crystals, contain irregularities the heights of which exceed the interatomic distances. For technological applications, both macro- and micro/nanotopography of the surfaces (surface texture) are important.

In addition to surface deviations, the solid surface itself consists of several zones having physico-chemical properties peculiar to the bulk material itself (Fig. 2.1.1) (Gatos, 1968; Haltner, 1969; Buckley, 1981). As a result of the forming process in metals and alloys, there is a zone of work-hardened or deformed material on top of which is a region of microcrystalline or amorphous

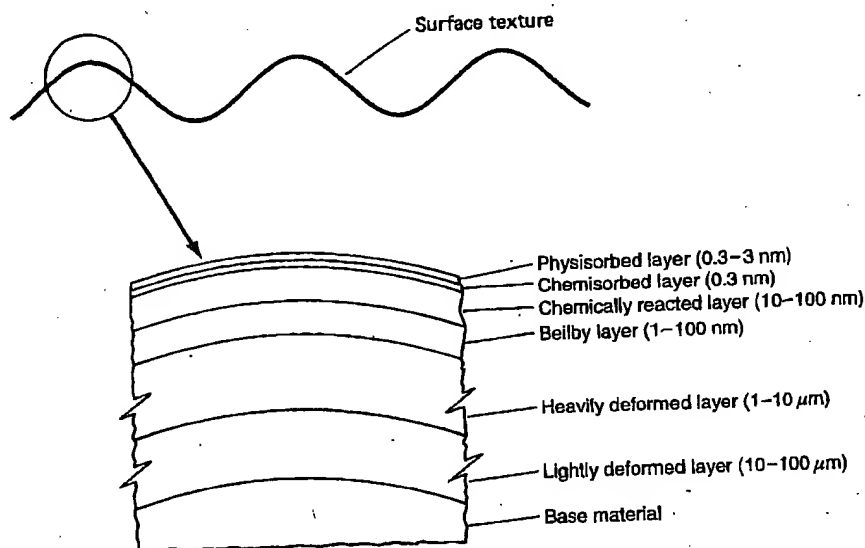**10   SOLID SURFACE CHARACTERIZATION**

Fig. 2.1.1 Solid surface details: surface texture (vertical axis magnified) and typical surface layers.

structure that is called the Beilby layer. Deformed layers would also be present in ceramics and polymers. These layers are extremely important because their properties, from a surface chemistry point of view, can be entirely different from the annealed bulk material. Likewise, their mechanical behavior is also influenced by the amount and depth of deformation of the surface layers.

Many of the surfaces are chemically reactive. With the exception of noble metals, all metals and alloys and many nonmetals form surface oxide layers in air, and in other environments they are likely to form other layers (for example, nitrides, sulfides, and chlorides). Besides the chemical corrosion film, there are also adsorbed films that are produced either by physisorption or chemisorption of oxygen, water vapor, and hydrocarbons, from the environment. Occasionally, there will be a greasy or oily film derived from the environment. These films are found both on the metallic and nonmetallic surfaces.

The presence of surface films affects friction and wear. The effect of adsorbed films, even a fraction of a monolayer, is significant on the surface interaction. Sometimes, the films are worn out in the initial period of running and subsequently have no effect. The effect of greasy or soapy film, if present, is more marked; it reduces the severity of surface interaction often by one or more orders of magnitude.

Besides the chemical reactivity of the surfaces and the tendency of molecules to adsorb on it, which are regarded as extrinsic properties of the surface, an important property that must be considered is surface tension or surface free energy. This affects the adsorption behavior of the surfaces. Details on different surface layers will be presented next followed by the analysis of surface roughness and measurement of surface roughness.

2.2 PHYSICO-CHEMICAL CHARACTERISTICS OF SURFACE LAYERS

2.2.1 Deformed Layer

The metallurgical properties of the surface layer of a metal, alloy or a ceramic can vary markedly from the bulk of the material as a result of the forming process with which the material surface was prepared. For example, in grinding, lapping, machining or polishing, the surface layers are plastically deformed with or without a temperature gradient and become highly strained. Residual stresses may be released of sufficient magnitude to affect dimensional stability. The strained layer is called the deformed (or work hardened) layer and is an integral part of the material itself in the surface region (Samuels, 1960; Bhushan, 1996; Shaw, 1997). The deformed layer can also be produced during the friction process (Cook and Bhushan, 1973).

The amount of the deformed material present and the degree of deformation that occurs are functions of two factors: (1) the amount of work or energy that was put into the deformation process, and (2) the nature of the material. Some materials are much more prone to deformation and work hardening than are others. The deformed layer would be more severely strained near the surface. The thickness of the lightly and heavily deformed layers typically ranges from 1 to 10 and 10 to 100 µm, respectively.

We generally find smaller grains in the deformed zone from recrystallization of the grains. In addition, the individual crystallite or grains with interface rubbing can orient themselves at the surface. The properties of the deformed layers can be entirely different from the annealed bulk material. Likewise, their mechanical behavior is also influenced by the amount and the depth of deformation of the surface layers.

2.2.2 Beilby Layer

The so-called Beilby layer in metals and alloys is produced by melting and surface flow during machining of molecular layers that are subsequently hardened by quenching as they are deposited on the cool underlying material. The layer has an amorphous or microcrystalline structure. This layer is present even in superfinished balls of ball bearings. Careful finishing procedures (lapping or wet polishing) can reduce the thickness of the Beilby layer. The thickness typically ranges from 1 to 100 nm.

2.2.3 Chemically Reacted Layer

With the exception of some noble metals (such as gold and platinum), all metals and alloys react with oxygen and form oxide layers in air; however, in other environments, they are quite likely to form other layers (for example, nitrides, sulfides, and chlorides) (Kubaschewski and Hopkins, 1953), Fig. 2.2.1.

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prepared under direction of the

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Specimens for Edge Retention, *Metal Prog*, Vol 90 (July 1966), p 103-104, 110

5. C. A. Johnson, Metallographic Sample Preparation, *AB Metal Digest*, Vol 11 (1965), No. 2, p 3-11

6. C. A. Johnson, The Effects of Pressure in Mechanical Polishing, *AB Metal Digest*, Vol 4 (1958), No. 3, p 2-10

7. P. Jacquet and P. Rocquet, Application of Electrolytic Polishing to Micrographic Examination of Iron and Steel (in French), *Compt Rend*, Vol 208 (Mar 1939), p 1012-1014

8. R. Pinner, Theory and Practice of Chemical Polishing: A Survey of Solutions and Processes for Various Applications, *Electroplating Metal Finishing*, Vol 7 (1954), p 127-131, 140

9. G. Schmid and H. Spähn, Chemical Polishing of Brass and German Silver. III. Chemistry of the Polishing Process (in German), *Z Metallk*, Vol 46 (1955), No. 2, p 128-137

10. G. Reinacher, Metallographic Preparation of Noble Metal Specimens by Electropolishing (in German), *Z Metallk*, Vol 48 (1957), p 162-170, 610-611

11. G. Reinacher, Metallographic Preparation of Noble Metal Specimens by Cutting With a Microtome (in German), *Z Metallk*, Vol 47 (1956), p 607-613

12. J. M. Dickinson, Polishing Hard Metals Electromechanically, *Metal Prog*, Vol 74 (Oct 1958), p 142-144

13. T. R. Padden and F. M. Cain, Jr., Cathodic Vacuum Etching, *Metal Prog*, Vol 66 (July 1954), p 108-112, 162, 164

14. F. Osmond, G. Cartaud and C. Frémont, Modes of Deformation and Rupture of Iron and Mild Steel (in French), *Rev Met (Paris)*, Vol 1 (1904), p 11

15. W. Shockley and W. T. Read, Quantitative Predictions from Dislocation Models of Crystal Grain Boundaries, *Phys Rev*, Vol 75(1) (1949), p 692

16. J. D. Livingston, Etch Pits at Dislocations in Copper, *J Appl Phys*, Vol 31 (June 1960), p 1071-1076

17. H. Kostron, Grain Coloration and Line Etching of Aluminum-Copper-Magnesium Alloys (in German), *Z Metallk*, Vol 39 (1948), p 333-342

18. W. Schatt, Texturblechkontrolle mit Hilfe der Schraffurätzung, *Prakt Metallographie*, Vol 4 (Dec 1967), p 620-625

19. S. A. Sved, Method of Exposing the Substructure of Silicon Electrical Steel, *Steel (USSR)*, Vol 12 (Dec 1961), p 916-918

20. E. Ostroff, Photo Fixing, *Photo Methods for Industry*, Vol 11 (Oct 1960), p 14

21. J. Dyson, A Unit-Magnification Optical System for the Attainment of Long Working Distances in Microscopy, *Proc Phys Soc (London)*, Vol 62(B) (1949), p 565-575

Principles of Technique Selection in Mechanical Polishing

By L. E. SAMUELS*

THREE distinct operations are involved in determining the microstructure of metals with the use of an optical microscope: (*a*) preparation of a section surface; (*b*) development of the structure on that surface, usually by chemical etching; and (*c*) microscopic examination. Unfortunately, the effectiveness of the examination often is determined by the operation carried out least effectively, and frequently this is surface preparation.

The attitude of many people that specimen preparation is tedious and an art probably is a result of the dearth of information based on systematic and objective experiments, and hence a result of a lack of understanding of the principles involved. One purpose of the present article is to illustrate how objective experiments and comparisons can be used to develop procedures that not only give better results but also are simpler and less laborious to use. The emphasis will be on principles that can be used as guides in the development of practical preparation procedures, rather than on the details of those procedures.

A primary objective of a preparation procedure must be to produce a surface that fully represents the microstructure as it existed in the metal before sectioning. All structural features characteristic of the metal must be detectable, and false structures must not be introduced. This is a more demanding requirement than the mere production of a highly polished surface.

Because it is possible to deal here with only a limited number of concepts involved in preparing fully representative surfaces, the concepts selected should be regarded as illustrations of the types of problems that arise and

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how their solution may be approached in a systematic way. In particular, it is not possible to discuss in detail the mechanisms by which abrasion (or grinding) and polishing processes operate. It must suffice to say that the abrasive points that contact the surface may be regarded as V-point cutting tools. The rake angles of these tools vary over a wide range; many are highly negative. Only a small proportion of abrasive points have a configuration suitable for removing metal by cutting a chip, as in normal machining; the others plough a groove in the surface, displacing metal laterally. Both processes impose severe plastic deformation.

Abrasion Damage and Abrasion Artifacts

It is convenient to divide the stages of metallographic preparation discussed in this article into two groups: (*a*) those employing fixed abrasives (such as abrasive papers and laps), which can be called abrasion (or grinding) processes; and (*b*) those in which the abrasive is suspended in a liquid held on a cloth pad, which can be called polishing processes. Abrasion processes are employed during the early stages of metallographic preparation and are intended to produce a flat surface with a reasonably fine finish. Polishing processes are employed to produce surfaces with ultrafine finishes that are suitable for final examination.

The obvious result of abrasion is a system of comparatively fine, uniform scratches on the surface of the specimen. In addition, however, abrasion also produces a plastically deformed surface layer (disturbed metal) of considerable depth, and the microstructure of this layer may be recognizably different from the true structure of the specimen.

The general pattern of a surface layer that has been plastically deformed is shown in micrograph 2825†, of abraded 70-30 brass, an alloy in which the effects of prior plastic deformation can readily be revealed by a range of etchants. Micrograph 2825 illustrates several characteristic features. The shallow, dark-etching, unresolved band contouring the surface scratches is known as the outer fragmented layer; it is a layer in which the strains have been very large. Beneath this extends a layer in which the strains have been comparatively modest and in which they tend to concentrate in rays extending beneath individual surface scratches. This is shown by the bands of etch markings, which are known to develop at the sites of slip bands, and by the more diffuse rays, which are known to indicate the presence of kink bands. These effects extend for many times the depth of the surface scratches.
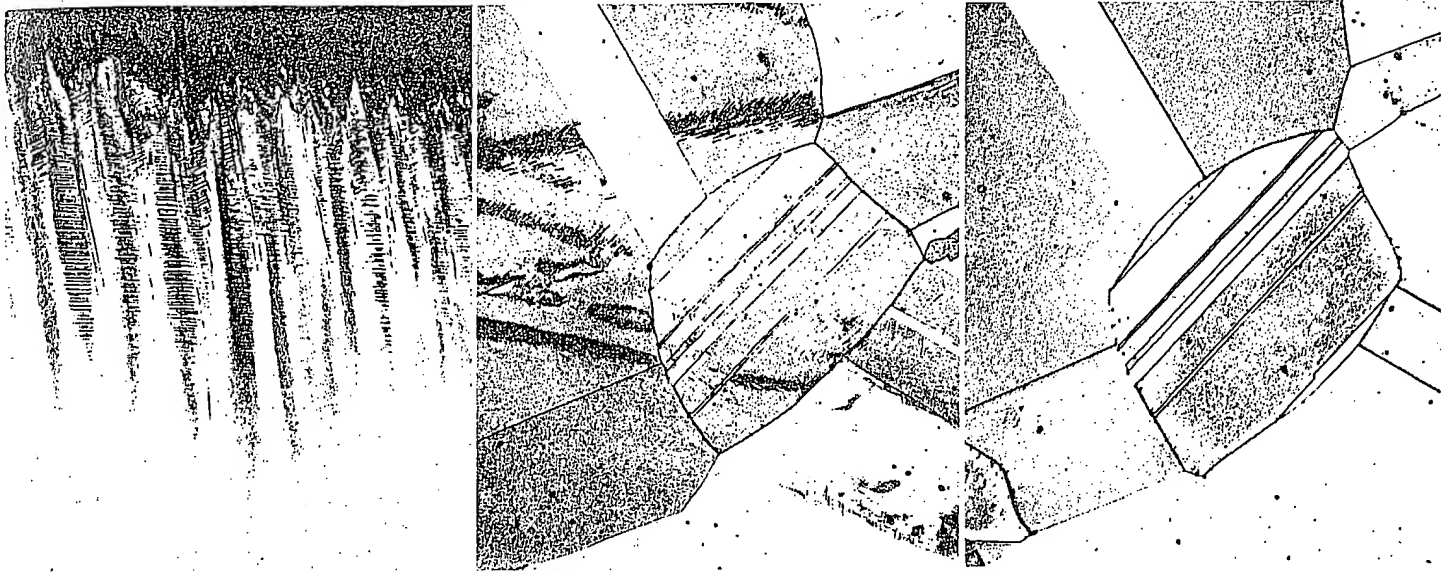
The importance of the surface damage in micrograph 2825 is illustrated by micrographs 2826 and 2827. A sample of annealed 70-30 brass was abraded on 220-grit silicon carbide paper and then polished to remove a surface layer about 5 microns thick. All traces of the abrasion scratches were removed and, ostensibly, a satisfactory surface was produced, but the bands of deformation etch markings shown in micrograph 2826 appeared when the surface was etched. When layers of greater thickness were removed during polishing, these bands were gradually reduced in number and intensity, and eventually were eliminated, as can be seen in micrograph 2827, which shows the true structure.

The bands of deformation etch markings in micrograph 2826 are false structures introduced by the preparation process, or artifact structures. They clearly are related to the rays of deformation produced during abrasion, as shown in micrograph 2825. Because the artifacts are without doubt the result of deformation introduced into the surface during abrasion, they may be called abrasion artifacts.

†Micrograph 2825 shows a taper section in which the apparent magnification in depth (vertically in the micrograph) is 8.2 times the nominal magnification. Here, the section line is perpendicular to a set of unidirectional abrasion scratches. Similar taper sections are shown in micrographs 2828, 2831, 2835, 2844, 2862, 2876 and 2877. When the section line is parallel to the abrasion scratches (as in micrographs 2839, 2840, 2850, 2851 and 2852), the section is referred to as a longitudinal taper section.

Aqueous ferric chloride   600 and 4920×   Aqueous ferric chloride   250×   Aqueous ferric chloride   250×

2825, 2826, 2827   Annealed 70-30 brass. **Micrograph 2825 (left)** shows a taper section (horizontal magnification 600×, vertical magnification 4920×) of surface layers that were abraded on 220-grit silicon carbide paper. The structures shown are discussed in the text. **Micrographs 2826 and 2827 (center and right)** show the results of abrading on 220-grit silicon carbide paper and then polishing until about 5 microns (micrograph 2826) and 15 microns (micrograph 2827) of metal are removed. The banded markings in micrograph 2826 are false structures (abrasion artifacts). Micrograph 2827 shows the true structure.

Electrolytic: oxalic acid   600 and 6060×   Electrolytic: oxalic acid   500×   Electrolytic: oxalic acid   500×

2828, 2829, 2830   Austenitic stainless steel (18% Ni, 8% Cr). **Micrograph 2828 (left)** shows a taper section (horizontal magnification 600×, vertical magnification 6060×) of surface layers that were abraded on 220-grit silicon carbide paper. The structures shown are discussed in the text. **Micrographs 2829 and 2830 (center and right)** show the results of abrading on 600-grit silicon carbide paper and polishing until about 1 micron (micrograph 2829) and 3 microns (micrograph 2830) of metal are removed. Micrograph 2829 shows abrasion artifacts. Micrograph 2830 shows the true structure.

Detectable microstructural changes in the abrasion-damaged layer are potential sources of abrasion artifacts in the final surface. Metals vary markedly in their susceptibility to the formation of abrasion artifacts (highly alloyed copper alloys, such as 70-30 brass, are among the most sensitive). Etchants also vary in their ability to delineate abrasion damage. Because a major objective of metallographic preparation is to ensure that unrepresentative structures are not present in the surface to be examined, the metallographer must learn to recognize abrasion artifacts, must understand how these artifacts originate, and must be able to take appropriate corrective action to eliminate

them when they are found. These concepts define some of the principles of a satisfactory preparation technique, including the following:

1 Each successive abrasion stage should remove the artifact-containing layer produced by the preceding abrasion stage. This will take much longer than the time required simply to remove preexisting scratches.
2 The effectiveness of an abrasion stage must be judged on how quickly it removes the preexisting deformed layer, and the depth of damaged layer that it itself produces, as well as on the more obvious criterion of the depth of the scratches that it produces.
3 Likewise, the first objective of the rough-polishing stage must be effective removal of abrasion damage. This places a pre-

mium on fast removal of material. The polishing processes with fast cutting rates usually produce comparatively coarse finishes. They must be followed by polishing processes that produce finer finishes. Only after the abrasion damage has been removed effectively by a rough-polishing process should attention be given to producing a final polish.

Abrasion Artifacts in Austenitic Steels. Austenitic steels generally are quite susceptible to abrasion artifacts, and the common etchants reveal effects due to prior deformation with considerable sensitivity. The structure of a typical abrasion-damaged layer (see micrograph 2828) is comparable to that for brass. A shallow, unresolved layer contours the surface scratches, and deep

rays of deformation. etch markings extend beneath the surface scratches. Bands of these deformation etch markings may appear in a final-polished surface as abrasion artifacts (see micrograph 2829). Good abrasion practice and efficient polishing processes are required for removal of the abrasion artifacts in acceptable polishing time (see micrograph 2830).

When a surface is found to contain artifacts of the type shown in micrograph 2829, it can be assumed that a surface layer of considerable depth will have to be removed before an artifact-free surface will be obtained. Therefore, the specimen must be returned to rough polishing in order to obtain a sufficiently high cutting rate. Alternate polishing and etching at the final-polishing stage, as is sometimes recommended, is not likely to be particularly effective.

Abrasion Artifacts in Zinc. Metals of noncubic crystal structure, such as zinc, characteristically form massive mechanical twins during plastic deformation. This is reflected in the abrasion-damaged layer in micrograph 2831, where

deformation twins are present to considerable depth. In metals having low melting points, such as tin and zinc, recrystallization of the deformed structure may also occur at ambient temperature; this accounts for the fact that the outermost portion of the abrasion-damaged layer in micrograph 2831 is recrystallized. The grain size of a recrystallized layer usually is quite fine, and becomes finer as the surface is approached; only by coincidence will the grain size be similar to that of the parent metal.

The following range of artifact structures may be observed if an abraded surface of zinc is polished for progressively longer times:

1 A fully recrystallized structure of different grain size from the parent metal (micrograph 2832)
2 A mixed structure of recrystallized grains and parent-metal grains containing deformation twins
3 Parent-metal grains containing deformation twins that are likely to be aligned in bands in the direction of the initiating abrasion scratches (micrograph 2833).

When polishing has been continued long enough for removal of the abra-

sion-damaged layer, the true structure may be observed (micrograph 2834).

Efficient preparation procedures depend on avoiding the production of deep abrasion-damaged layers prior to polishing, and thereby avoiding the need for removing them by excessive polishing.

Abrasion Artifacts in Ferritic Steels. The deep abrasion-damage effects discussed thus far cause difficulties in only a limited range of alloys, but effects due to an outer fragmented layer are likely to be found in all metals. A section of the outer fragmented layer in a ferritic steel is shown in micrograph 2835. The structure of the fragmented layer cannot be properly resolved by optical microscopy, but it is clear that the structure is different from that of the parent-metal ferrite grains. The types of artifacts that may be found in final-polished surfaces of ferritic steel are illustrated in micrographs 2836 and 2837. These artifacts obscure the true structure, shown in micrograph 2838; they can be developed in virtually all metals. However, as shown in micrograph 2835, the damaged layer is quite thin, and a polishing treatment con-
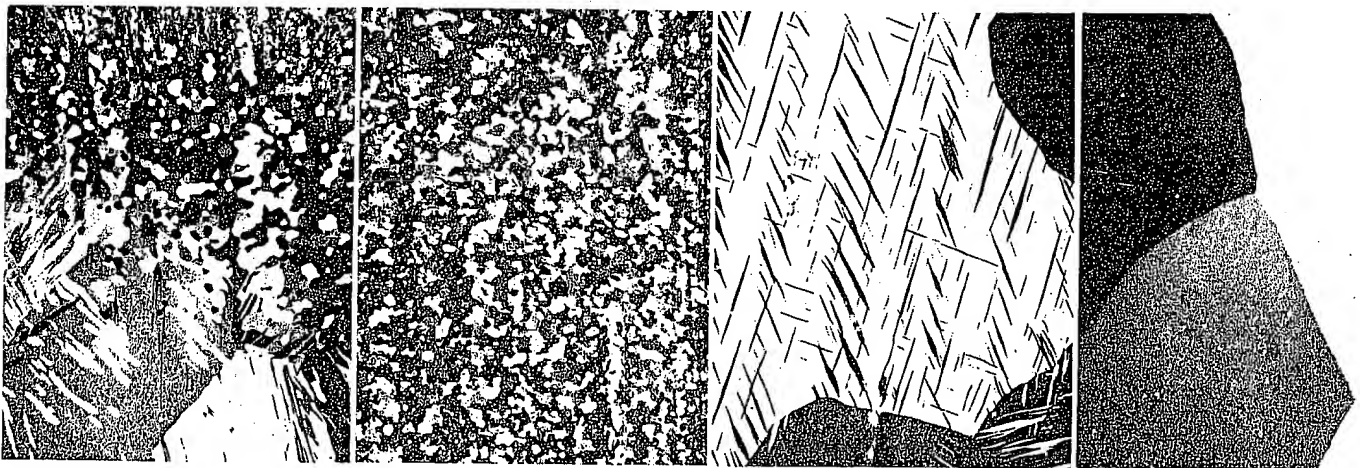
As polished   150 and 2040×   As polished   150×   As polished   150×   As polished   150×

2831, 2832, 2833, 2834 Annealed zinc. **Micrograph 2831** (left) shows a taper section (horizontal magnification 150×, vertical magnification 2040×) of surface layers that were abraded on 220-grit silicon carbide paper. Note recrystallization at the top. Polarized light was used. **Micrographs 2832, 2833 and 2834 (left-center, right-center and right)** show the results of abrading on 220-grit silicon carbide paper and polishing until 2.5 microns (micrograph 2832), 15 microns (micrograph 2833), and 45 microns (micrograph 2834) of metal are removed. The small grains in micrograph 2832 and the twins in micrograph 2833 are artifact structures. The true structure is shown in micrograph 2834.

Nital   1000 and 10,000×   Nital   250×   Nital   250×   Nital   250×

2835, 2836, 2837, 2838 Ferritic steel. **Micrograph 2835** (left) shows a taper section (horizontal magnification 1000×, vertical magnification 10,000×) of surface layers that were abraded on 220-grit silicon carbide paper. Note the outer fragmented layer. **Micrograph 2836** (left-center) shows the results of abrading on 000 emery paper and then polishing only long enough to remove abrasion scratches. **Micrograph 2837** (right-center) shows the results of abrading on 600-grit silicon carbide paper and polishing only long enough to remove abrasion scratches. Micrographs 2836 and 2837 show banded markings and generally confused structure. **Micrograph 2838** (right) shows the results of abrading on 600-grit silicon carbide paper and polishing for a longer time than for micrograph 2837; it shows the true structure of the steel.
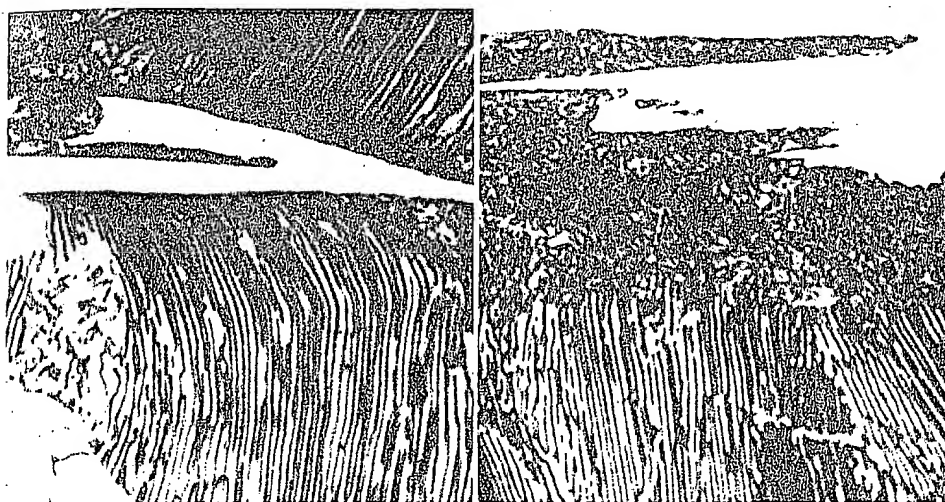
Picral   2000 and 20,000×   Picral   2000 and 20,000×

2839, 2840   Pearlitic steel. Longitudinal taper sections (horizontal magnification 2000×, vertical magnification 20,000×) of surface layers that were belt abraded on 100-mesh alumina, showing that cementite plates of pearlite are merely bent adjacent to some scratches (micrograph 2839, left) and are completely fragmented adjacent to others (micrograph 2840, right).

tinued for twice the time it takes to remove the abrasion scratches will eliminate the abrasion artifacts. Thus, structures with abrasion artifacts are usually the result of very inefficient preparation procedures.

Abrasion Artifacts in Pearlitic Steels. Certain distinctive artifacts caused by disturbance in the outer fragmented layer are observed in pearlitic steels. Taper sections of abraded surfaces of these steels show that the cementite plates of pearlite may simply be bent adjacent to some scratches (micrograph 2839) and may be completely fragmented adjacent to others (micrograph 2840). As a result, artifact structures of the types shown in micrographs 2841 and 2842 may be observed in surfaces after final polishing. The cementite plates in micrograph 2841 have been so fragmented that the pearlite structure is unrecognizable as such; the appearance, in fact, is more like that found after hardening and

tempering. The structure in micrograph 2842 is recognizable as lamellar pearlite, but the kinking of the cementite plates represents an artifact structure. The true pearlite structure, free of artifacts, is shown in micrograph 2843. The affected layer in micrographs 2841 and 2842 is quite shallow, and the artifacts shown are likely to be found only after inefficient preparation procedures.

Tempering Artifacts in Steel. When steels with medium to high carbon content are ground or abraded abusively, especially under conditions of an inadequate supply of coolant, the surface may be heated sufficiently to develop a rehardened martensitic surface layer, such as the outer white-etching layer shown in micrograph 2844. A martensitic layer is likely to be quite thin. If these steels initially are in the hardened-and-untempered condition, the rehardened layer will be accompanied by a tempered layer that is much deeper and highly variable in depth; the tem-

pered layer is dark etching. The bands of tempered structure (see micrograph 2845) are much more likely to give rise to artifact structures than the martensitic layer. The artifact structure is banded because the abrasion operation that caused the damage produced a system of unidirectional scratches. When compared to the true structure in micrograph 2846, it is apparent that artifact banding could easily be mistaken for segregation banding in steel. Similar effects may occur in any alloy system in which structural changes can result from reheating.

Tempering artifacts can be avoided by ensuring that the specimen is flooded with a copious supply of a liquid coolant during all abrasion operations, particularly those involving high speeds. Dry, mechanized abrasion processes should be avoided.

Abrasion Damage in Gray Iron. Cast irons represent an important group of alloys for which a purpose of metallographic examination often is the determination of the true size and shape of the particles of free graphite that are present. The apparent size and shape of the graphite can be severely altered at several stages of the preparation sequence, thus giving rise to false structures.

The true graphite form for a particular gray iron is most closely represented in micrograph 2849. This can be confirmed by examining a taper section of the surface (micrograph 2852), where it is seen that most of the graphite flakes are accurately sectioned; a few, those that were acutely aligned to the section surface, are slightly enlarged. On the other hand, the majority of flakes on a coarsely abraded surface appear to be much narrower than their true width (micrograph 2847), because the graphite has been removed from its cavity for a considerable depth and the empty portion of the cavity has collapsed (micrograph 2850). An intermediate abrasion treatment gives an intermediate result (micrograph 2848); the flakes in some areas are of true width and in others
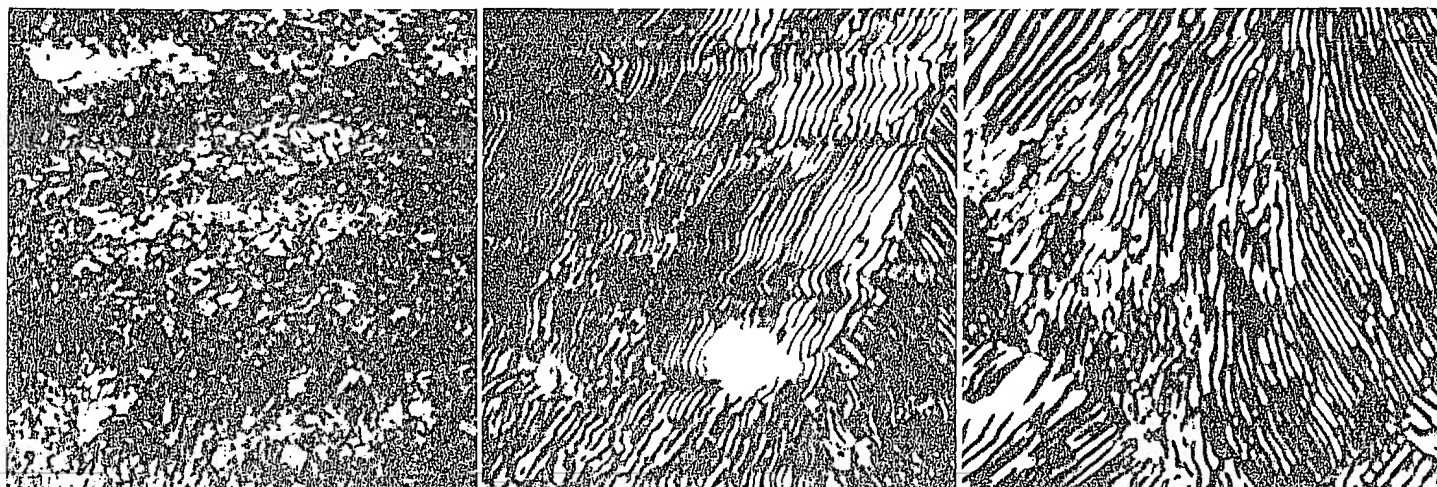

Picral   2000×   Picral   2000×   Picral   2000×

2841, 2842, 2843   Pearlitic steel. Micrograph 2841 (left) shows the results of abrading on an abrasive belt and then polishing for only long enough to remove abrasion scratches; structure contains abrasion-deformation artifacts. Micrograph 2842 (center) shows the results of abrading on 600-grit silicon carbide paper and then polishing only long enough to remove abrasion scratches; kinking of cementite plates is an abrasion-deformation artifact. Micrograph 2843 (right) shows the results of abrading on 600-grit silicon carbide paper and polishing for a longer time than for micrograph 2842; it shows the true structure.
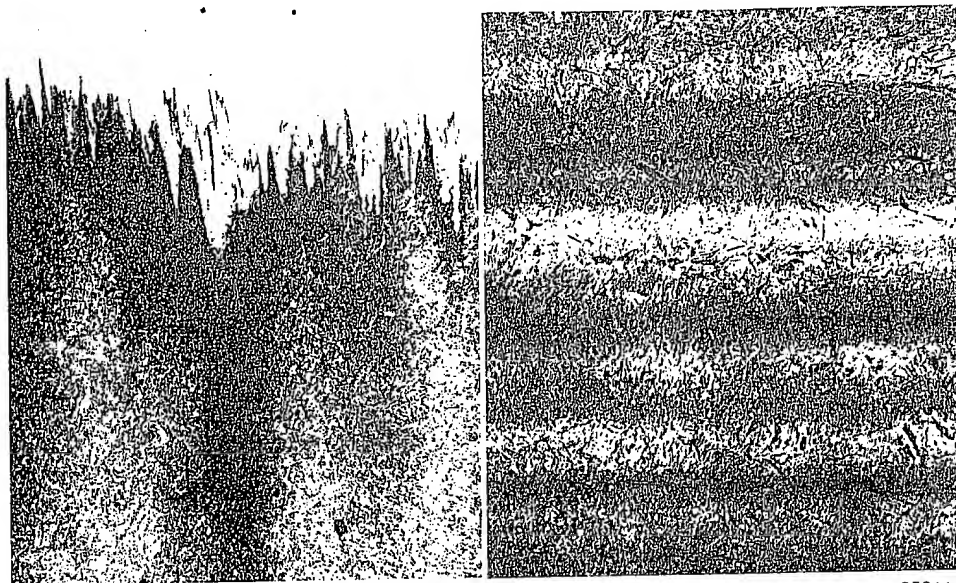
Picral   1200 and 13,080×   Picral   250×   Picral   250×

2844, 2845, 2846   Plain carbon steel, hardened but not tempered. **Micrograph 2844 (left)** shows a taper section (horizontal magnification 1200×, vertical magnification 13,080×) of surface layers that were abusively abraded, producing martensite (white-etching constituent) and tempering (dark-etching bands). **Micrograph 2845 (center)** shows dark-etching bands of tempered structure that originated from dry belt grinding. **Micrograph 2846 (right)** shows the true structure.
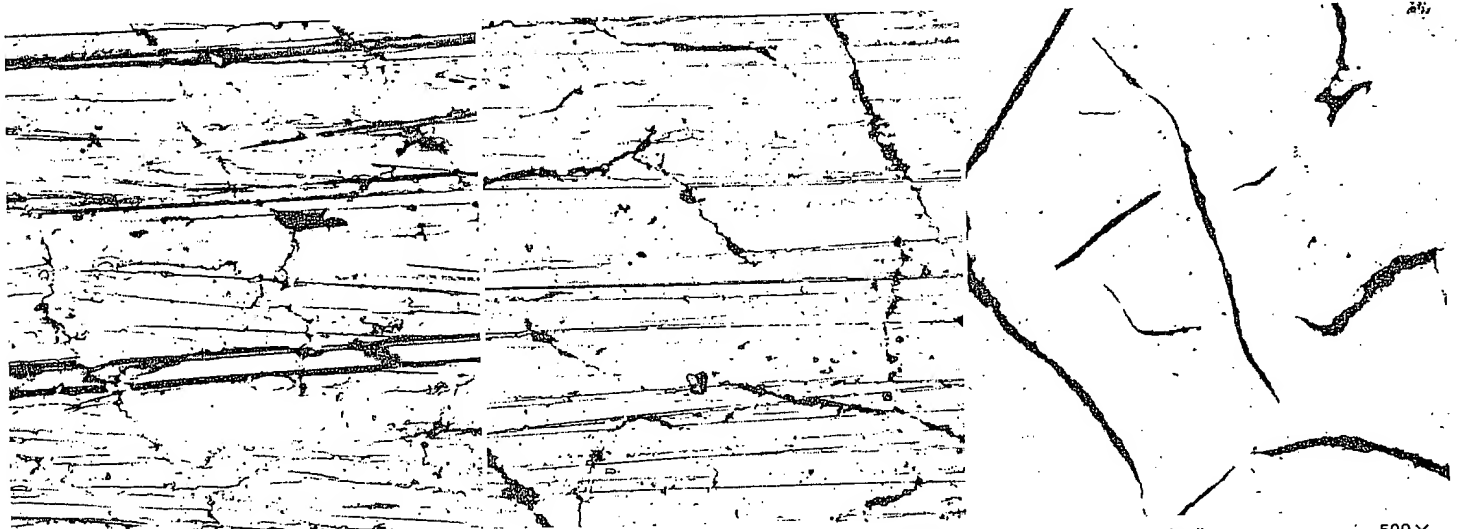
As polished (not etched)   500×   As polished (not etched)   500×   As polished (not etched)   500×

2847, 2848, 2849   Effects of abrasion on flake graphite in gray iron. **Micrograph 2847 (left)** shows results of abrading on 220-grit silicon carbide paper; **micrograph 2848 (center)**, on 600-grit silicon carbide paper; and **micrograph 2849 (right)**, on a fine fixed-abrasive lap. See also the taper sections in micrographs 2850, 2851 and 2852.
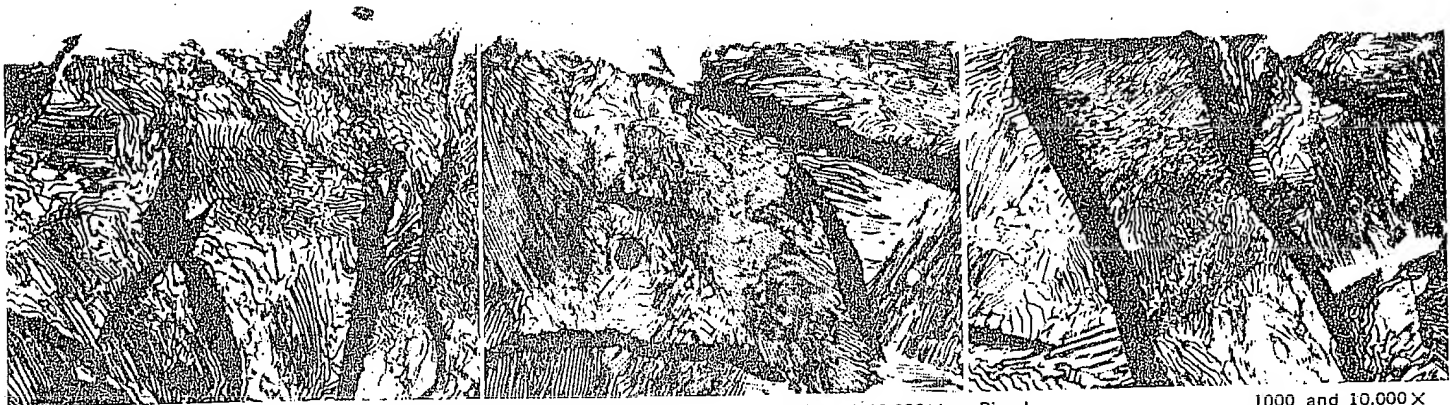
Picral   1000 and 10,000×   Picral   1000 and 10,000×   Picral   1000 and 10,000×

2850, 2851, 2852   Longitudinal taper sections of abraded surfaces in gray iron (horizontal magnification 1000×, vertical magnification 10,000×). **Micrograph 2850 (left)** shows results of abrading on 220-grit silicon carbide paper; **micrograph 2851 (center)**, on 600-grit silicon carbide paper; and **micrograph 2852 (right)**, on a fine fixed-abrasive lap.

are greatly contracted. On the other hand, the flakes appear to be much wider than their true width at occasional areas in both micrographs 2847 and 2848; this is because the graphite has been removed from its cavity and then the cavity has been enlarged (micrograph 2851), presumably by erosion.

Problems in preserving graphite correctly also arise during polishing, so that it is unwise to rely on subsequent polishing to correct damage introduced by abrasion. The objective of the abrasion stage should be to retain the graphite as fully as possible; in this respect, the use of fixed-abrasive laps is very beneficial.

Flatness of Abraded Surfaces. In many applications, finishing abrasion on a fixed-abrasive lap provides results that are more satisfactory than those obtained by finishing on abrasive papers. In general, a much flatter surface is obtained from a lap, resulting, for example, in improved preservation of edges (compare micrographs 2853 and 2854), improved retention of nonmetallic inclusions (compare micrographs 2855 and 2856), and reduction in the difference in level between different phases (compare micrographs 2857 and 2858). A somewhat finer finish is also obtained. However, because it is generally more difficult to use fixed-abrasive laps than abrasive paper, a value judgment is required to decide whether the improvement in finish is worth the additional effort.

Embedding of Abrasive. The points of the contacting abrasive particles of an abrasive paper fracture readily during abrasion, and these fragments may become embedded in the surface of a very soft metal, such as lead or annealed high-purity aluminum. Embedded particles are difficult to discern in the surface by optical microscopy, but a surface with a high concentration of embedded abrasive characteristically has a rough, torn appearance (micrograph 2859), quite different from the regular grooves of a normal abraded surface. It is very difficult to prepare such a surface through subsequent stages.

Embedding of abrasive fragments can be avoided by filling the surface of the abrasive paper with a soft wax; then the fragments embed in the wax rather than in the specimen. The result of finishing high-purity lead on a silicon carbide paper lubricated with wax is shown in micrograph 2860. The surface of soft metals may also be prepared by cutting with a heavy microtome. This produces the highest-quality surface of all, as shown in micrograph 2861.

Polishing Damage

The mechanical polishing procedures commonly used in metallographic practice remove metal by mechanical cutting processes analogous to those occurring during abrasion. This type of mechanical polishing always produces a series of scratch grooves on the surface of the specimen; these scratches are difficult to detect by optical microscopy, particularly with bright-field illumination. Moreover, a plastically deformed, damaged layer is also introduced; the layer
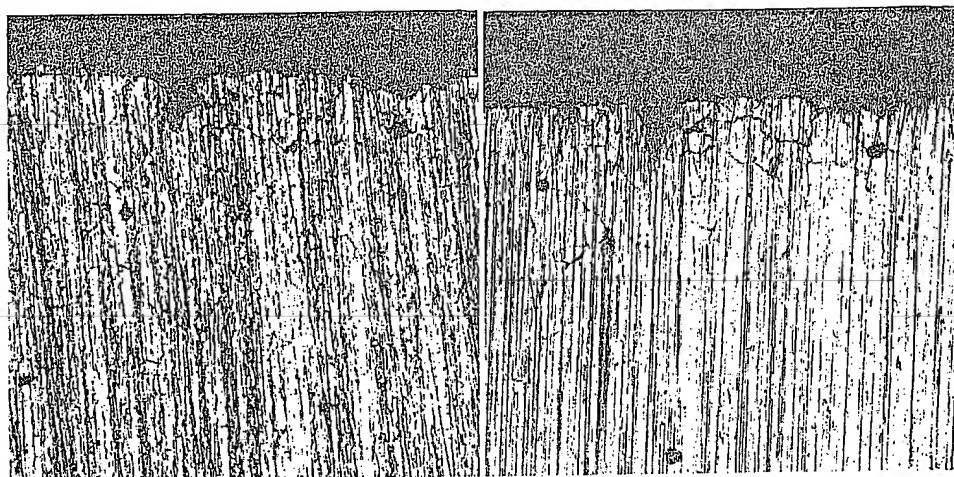
As polished (not etched)   100×   As polished (not etched)   100×

2853, 2854 Comparison of abrasives for preservation of corroded surface of aluminum alloy. **Micrograph 2853 (left)** shows results of abrading on 600-grit silicon carbide paper. **Micrograph 2854 (right)** shows the improvement in edge preservation obtained by abrading on a fine fixed-abrasive lap.
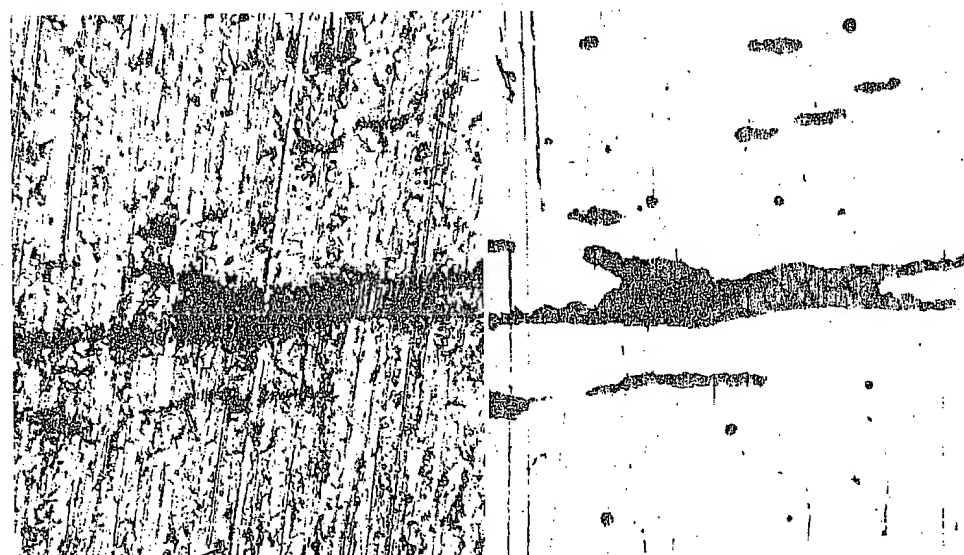
As polished (not etched)   500×   As polished (not etched)   500×

2855, 2856 Comparison of abrasives for preservation of a nonmetallic inclusion in wrought iron. **Micrograph 2855 (left)** shows results of abrading on 600-grit silicon carbide paper. **Micrograph 2856 (right)** shows the improved results obtained by abrading on a fine fixed-abrasive lap.
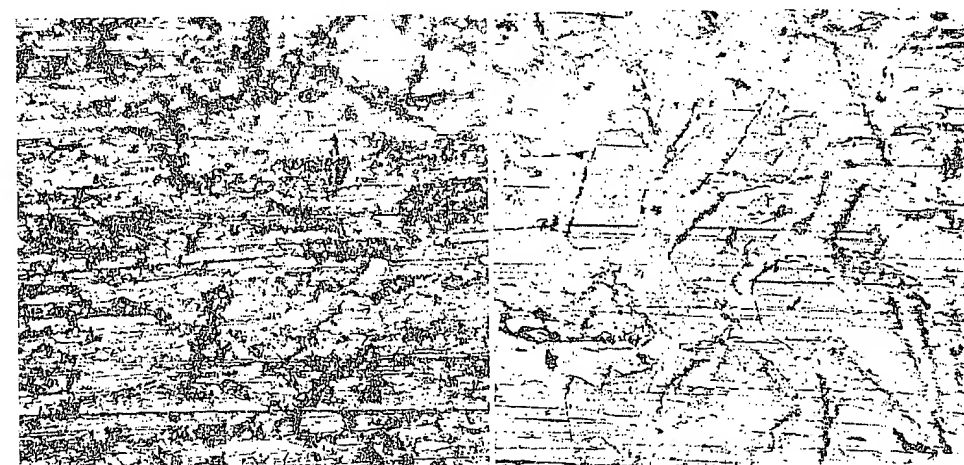
As polished (not etched)   250×   As polished (not etched)   250×

2857, 2858 Comparison of abrasives for reduction of the differences in level of different phases in Al-13Si alloy. **Micrograph 2857 (left)** shows results of abrading on 600-grit silicon carbide paper. **Micrograph 2858 (right)** shows the improved results obtained by abrading on a fine fixed-abrasive lap.

is much shallower than that produced by abrasion, but its structure is similar. Compare, for example, the damaged layer produced on the surface of annealed 70-30 brass by polishing (micrograph 2862) with that produced by abrading (micrograph 2825). A layer, analogous to the outer fragmented layer in abraded surfaces, can be recognized contouring the surface scratches, and there are occasional rays of deformed metal extending to greater depths, many times the depth of the polishing scratches. The presence of this damaged layer has important practical consequences — it affects the response of the surface to etching.

The presence of a damaged layer cannot be avoided by the use of polishing procedures in which the abrasive, no matter how fine, is suspended in a liquid that is comparatively inactive chemically with respect to the speci-

men. Sometimes, either intentionally or unintentionally, the liquid may be chemically active and a chemical-removal mechanism will then dominate, in which case a damaged layer may not be produced. Under these circumstances, the function of the abrasive appears to be that of removing protective films continuously, thus ensuring more uniform and more rapid chemical attack. This combination of action may be referred to as a mechanical-chemical polishing mechanism.

An excessive chemical component in a mechanical-chemical process may cause detrimental effects, such as severe etch pitting. Proper balance between the mechanical and chemical components can preserve most of the benefits provided by mechanical polishing and yet produce a damage-free surface — which is a most desirable combination in a final-polishing stage.

Degradation of Etching Contrast. The grain orientation of the section shown in micrograph 2862 is such that the section should etch light under the etching conditions indicated; however, etching is dark because of the presence of a dark-etching damaged layer. Also, as a consequence of the damaged layer, the grain contrast developed during etching is poor, as shown in micrograph 2863. This phenomenon can be expected whenever an etchant develops contrast by differential coloring; it may be described as a polishing artifact. Micrographs 2864 and 2865 present another example of the effect of polishing damage on response to etching.

Scratch Traces. If we subject a surface to coarse polishing and follow by finer polishing, and continue the finer polishing until the first series of scratches has been removed, but not until all the rays of deformation in the
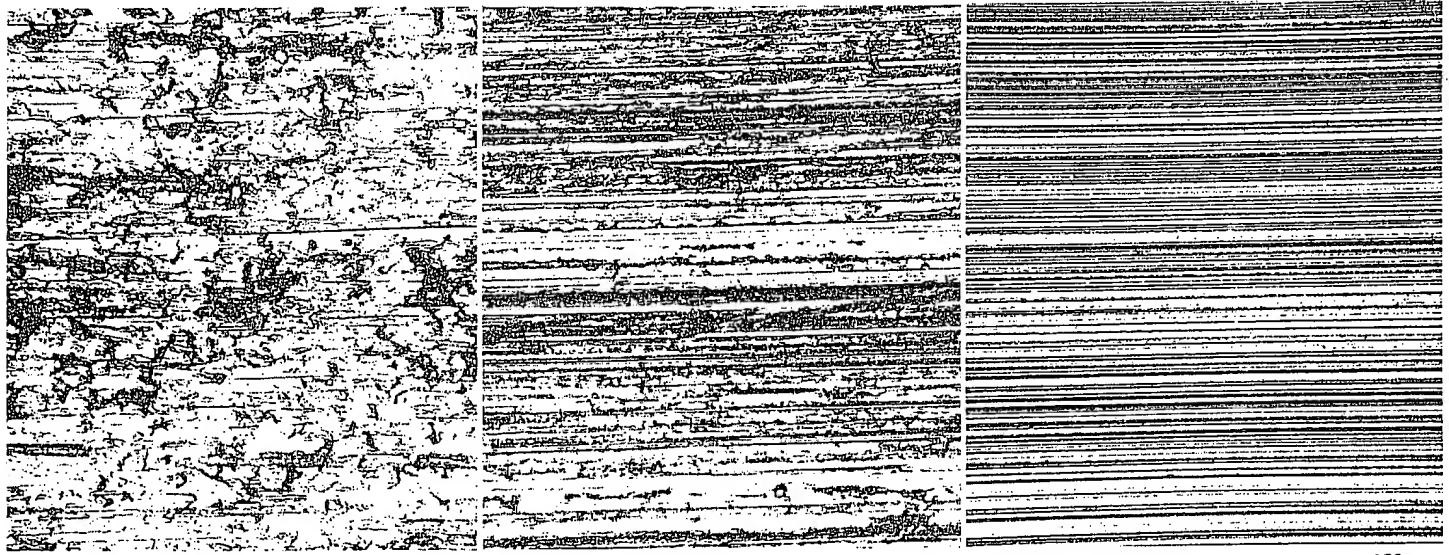
As polished (not etched)   250×   As polished (not etched)   250×   As polished (not etched)   250×

2859, 2860, 2861   Comparison of results obtained by finishing high-purity lead on 600-grit silicon carbide paper using water as the lubricant (**micrograph 2859, left**), on 600-grit silicon carbide paper using wax as the lubricant (**micrograph 2860, center**), and using a sledge microtome (**micrograph 2861, right**).
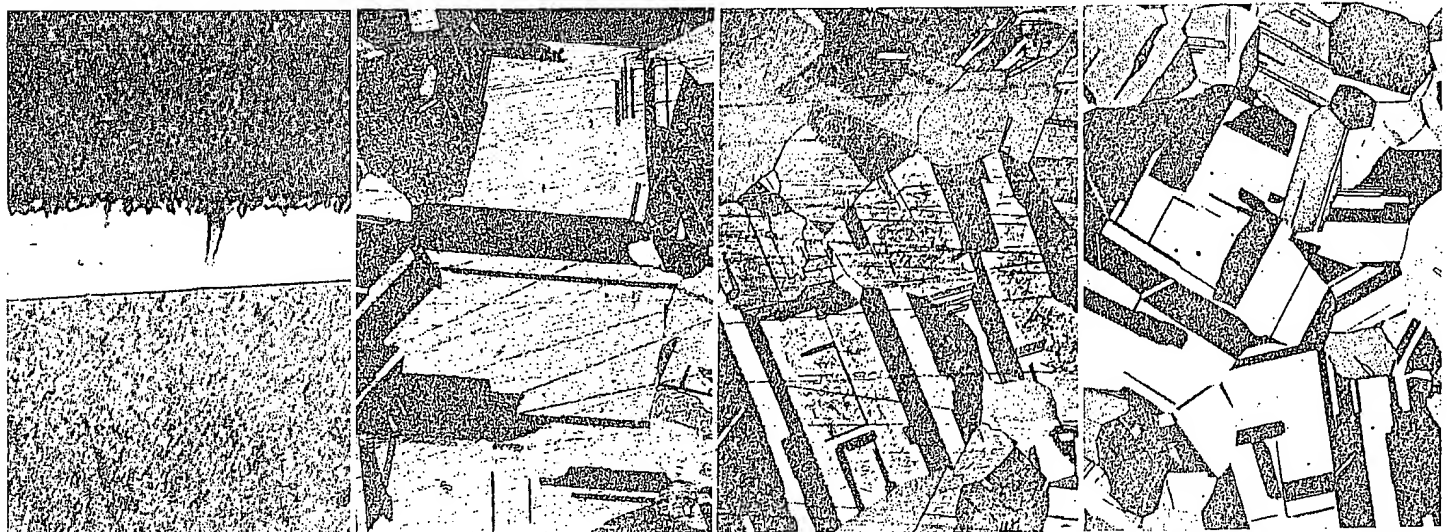
Aqueous FeCl₃   2000 and 21,800×   Aqueous ferric chloride   250×   Aqueous ferric chloride   250×   Aqueous ferric chloride   250×

2862, 2863, 2864, 2865   Effect of polishing damage on response to etching for annealed 70-30 brass. **Micrograph 2862** (left) shows a taper section (horizontal magnification 2000×, vertical magnification 21,800×) of surface layers that were polished on 1-micron diamond abrasive. The other micrographs show results of: etching immediately after polishing on 1-micron diamond abrasive (**micrograph 2863, left-center**); fine polishing for a short time before etching (**micrograph 2864, right-center**); and fine polishing for a longer time before etching (**micrograph 2865, right**).
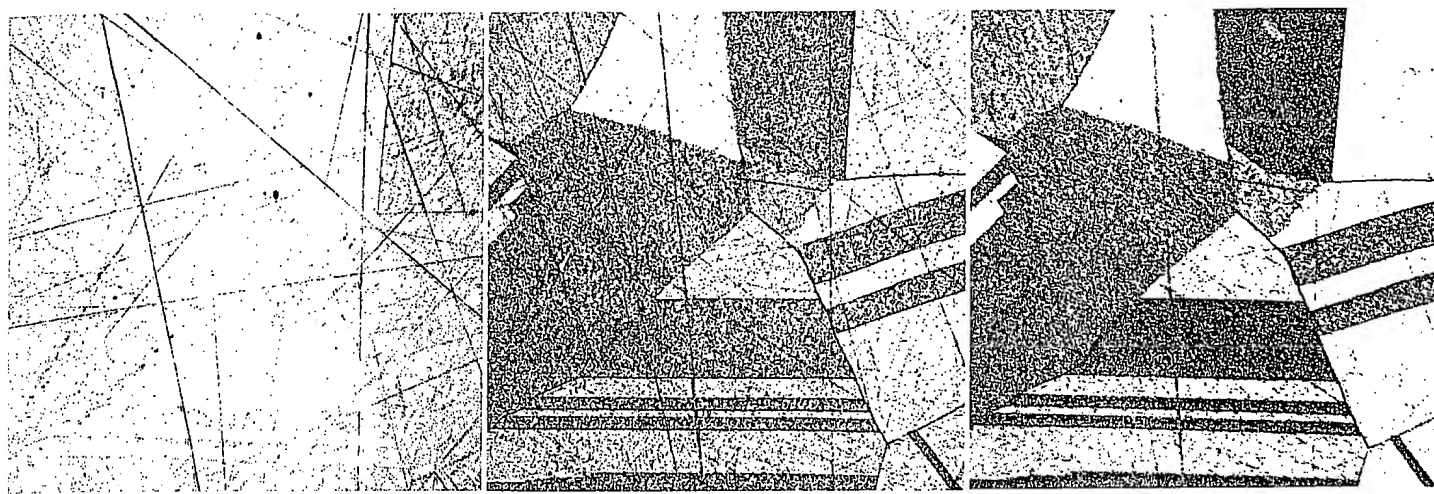
Aqueous ferric chloride   250×   Aqueous ferric chloride   250×   Aqueous ferric chloride   250×

2866, 2867, 2868 Effect of incremental increases in etching time (micrographs 2866, 2867 and 2868, left to right) on appearance and disappearance of scratches on a specimen of annealed 70-30 brass that was polished on fine alumina. Micrograph 2868 shows that a longer etching time removes scratches and the damaged layer.

layer damaged by polishing have been removed, the residuals of the rays of deformation left in the surface may be preferentially attacked during etching, as shown in micrograph 2864, giving the impression that some of the first series of scratches have reappeared. A surface free from these effects would be obtained if the finer polishing had been continued for a long enough time to remove all of the preexisting polishing damage, as shown in micrograph 2865.

This phenomenon is common in metallographic practice, and is frequently ascribed to the reappearance of the scratches themselves. However, the features developed should be thought of as "ghosts" of the original scratches; they are not the grooves of the original scratches. They may more properly be termed scratch traces, another type of polishing artifact.

Enlargement of Polishing Scratches by Etching. It is a frequent annoyance in metallographic practice to find that a surface that appeared to be free of scratches when examined as-polished under bright-field illumination turns out to be severely scratched after etching (see examples in micrographs 2866, 2867 and 2868). The scratches were actually there all the time, but they were too fine to be detected when the specimen was in the unetched condition; they were enlarged, or shown in greater contrast, by etching.

Scratches are attacked preferentially during etching because of the disturbed metal, or damaged layer, associated with them. Severity of attack varies directly with the ability of the etchant to reveal deformation. The appearance of scratches also depends on the etching time. A certain minimum etching time is necessary to develop the scratches fully; thereafter, the scratches recede with increasing etching time, because etching progressively removes the damaged layer.

It may be difficult to distinguish scratches enlarged by the final polishing stages from scratch traces introduced during the previous polishing stage. The problem can be resolved by making the earlier set of scratches unidirectional and parallel to a known di-


As polished (not etched)   350×   As polished (not etched)   350×

2869, 2870 Comparison of polishing methods for showing inclusions in wrought iron. For micrograph 2869 (left), specimen was polished on 10-to-20-micron alumina on billiard cloth; for micrograph 2870 (right), it was polished on 4-to-8-micron diamond on a synthetic suede cloth. Specimens in both micrographs were abraded on a fixed-abrasive lap before polishing.
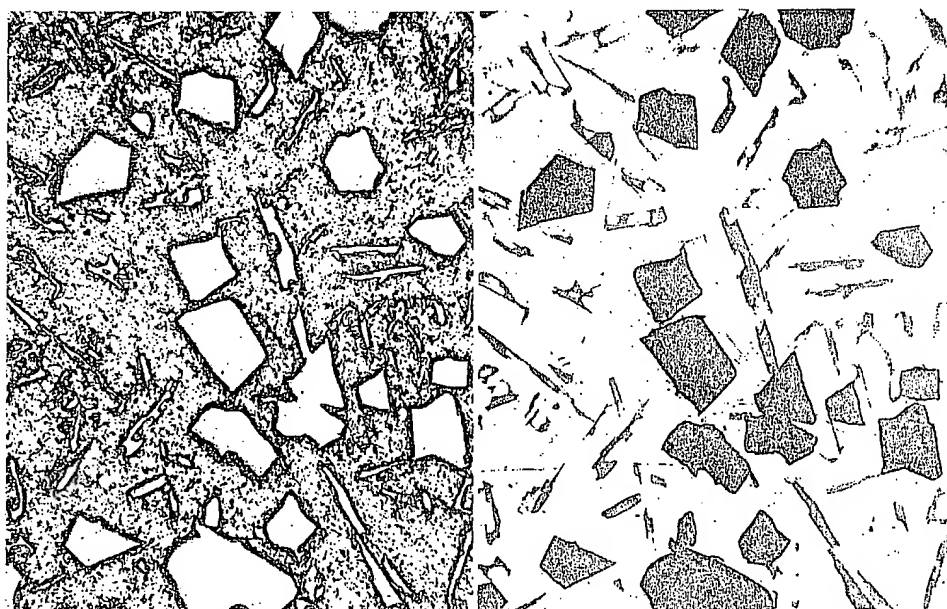
As polished (not etched)   250×   As polished (not etched)   250×

2871, 2872 Comparison of polishing methods for showing phases in Al-13Si alloy. For micrograph 2871 (left), specimen was polished on 10-to-20-micron alumina on billiard cloth; for micrograph 2872 (right), it was polished on 4-to-8-micron diamond on a synthetic suede cloth. Specimens in both micrographs were abraded on a fixed-abrasive lap before polishing.

As polished (not etched)   250×   As polished (not etched)   250×   As polished (not etched)   250×

2873, 2874, 2875   Comparison of polishing methods for retention. of graphite in gray iron. **Micrograph 2873 (left)** shows the results of polishing on 10-to-20-micron alumina on billiard cloth (long nap). **Micrograph 2874 (center)** shows the results of polishing on 1-micron diamond on synthetic suede cloth (short nap). **Micrograph 2875 (right)** shows the results of polishing on 1-micron diamond on cotton drill (napless). All specimens were abraded on a fixed-abrasive lap before polishing.
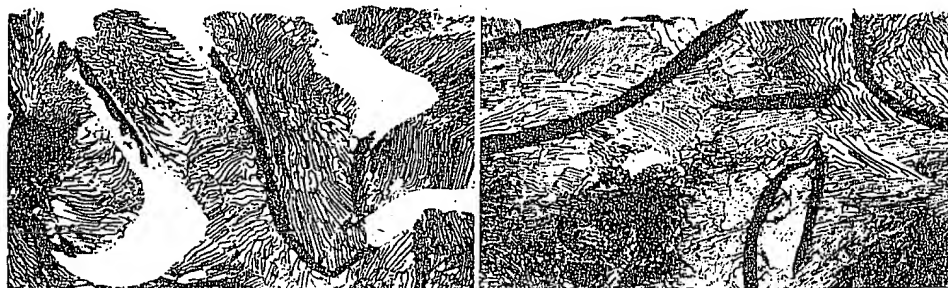
Picral   1000 and 10,000×   Picral   1000 and 10,000×

2876, 2877   Taper sections (horizontal magnification 1000×, vertical magnification 10,000×) comparing polishing methods for retention of graphite in gray iron. **Micrograph 2876 (left)** shows results of polishing on 10-to-20-micron alumina on billiard cloth (long nap). **Micrograph 2877 (right)** shows results of polishing on 1-micron diamond on synthetic suede (short nap).

rection in the specimen surface. The scratch traces can then be recognized. This technique was used in preparing the specimen for micrograph 2864.

Flatness. Quality in polishing practice means (a) a surface that is adequately free from confusing polishing scratches, and (b) a surface that is sufficiently flat for all constituents and local regions to be examined properly.

Two examples of how markedly the choice of polishing abrasive and polishing cloth can affect surface flatness in specimens of duplex structure are given in micrographs 2869 through 2872. These micrographs show that alumina abrasive on billiard cloth produced a result inferior to diamond abrasive on synthetic suede cloth in polishing wrought iron and an aluminum alloy. The alumina on billiard cloth produced marked relief between the silicon constituent and the aluminum matrix of the aluminum alloy (micrograph 2871) and removed a portion of the silicate inclusion in the wrought iron (micrograph 2869). These are not the only types of polishing cloths available, but the examples demonstrate the wide variation in quality of results that is possible, and the type of systematic

experiment that can be carried out to compare different polishing processes.

Retention of Graphite in Gray Iron. Earlier in this article, it was demonstrated that although the graphite in cast iron can be damaged severely during the abrasion stage of preparation, it is possible by suitable choice of abrasion process to obtain a reasonably true representation of the structure. There remains the problem of retaining the graphite during polishing. The solution to the problem depends heavily on the length of the nap of the polishing cloth.

Graphite flakes in a gray iron invariably look much larger when long-nap cloths are used for polishing, as demonstrated in micrograph 2873. This apparent enlargement is caused by erosion, which occurs at the interface between graphite and matrix, producing an enlarged cavity from which the flake itself eventually is removed (see micrograph 2876). With a cloth of reasonably short nap, many of the flakes are well retained, although some appear slightly larger (see micrographs 2874 and 2877). Examination of sections of such a surface indicates that flakes aligned perpendicular to the surface

are well sectioned (flakes at right in micrograph 2877) but that slight erosion occurs around flakes that happen to be acutely aligned to the section surface (flake at left in micrograph 2877). Correct representation of the graphite flakes is obtained after polishing with a napless cloth, as shown in micrograph 2875.

Only a limited number of abrasives, notably diamond abrasives, produce satisfactory results on napless cloths. Even then, a fairly heavily scratched polish is obtained. If this finish is not acceptable, a finishing treatment with a fine abrasive on a napped cloth is necessary. The treatment must be kept brief to avoid enlargement of the cavities.

Elimination of Polishing Scratches. Only rarely is it required that final-polished surfaces be completely free of scratches. A more reasonable and practical requirement is that no scratches should be detectable under the particular conditions of examination. Attainment of this objective will thus depend on the specimen material (more difficult with soft materials), the etching conditions (more difficult with etchants that are sensitive to deformed structures), and the optical conditions (more difficult with optical conditions that are sensitive to surface irregularities). In general, high-standard polishing processes are more laborious and require greater operator skill. A metallographer should have available a variety of final-polishing processes capable of producing increasingly higher qualities of finish from which to select the most suitable for a particular need.

The available range of polishing processes is represented by the series of micrographs 2878 through 2881. Note there that none of the mechanical polishing processes used (micrographs 2878, 2879 and 2880) produced a completely scratch-free surface, but that this was achieved by a mechanical-chemical technique (micrograph 2881). The mechanical-chemical technique was the
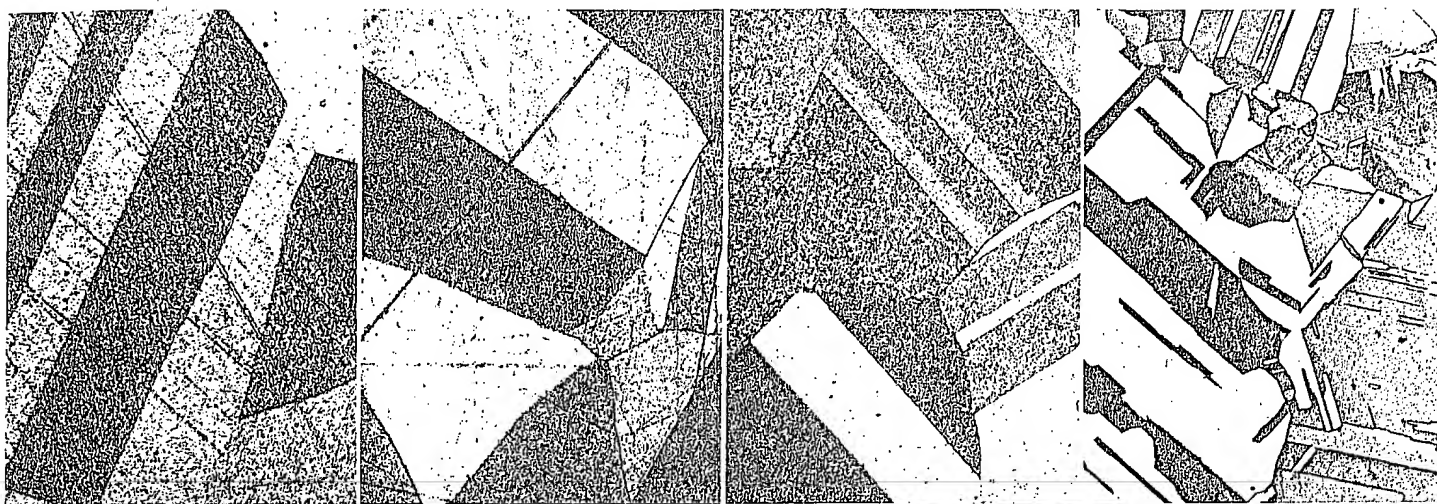
Aqueous ferric chloride   250×   Aqueous ferric chloride   250×   Aqueous ferric chloride   250×   Aqueous ferric chloride   250×

2878, 2879, 2880, 2881 Comparison of polishing methods for elimination of scratches in final polishing of annealed 70-30 brass. **Micrograph 2878 (left):** polishing on 1-micron diamond using standard mechanical technique. **Micrograph 2879 (left-center):** polishing on 0.1-micron alumina using standard mechanical technique. **Micrograph 2880 (right-center):** polishing on magnesia using standard mechanical technique. **Micrograph 2881 (right):** polishing on magnesia using mechanical-chemical technique. Note progressive improvement in scratch-elimination from left to right.
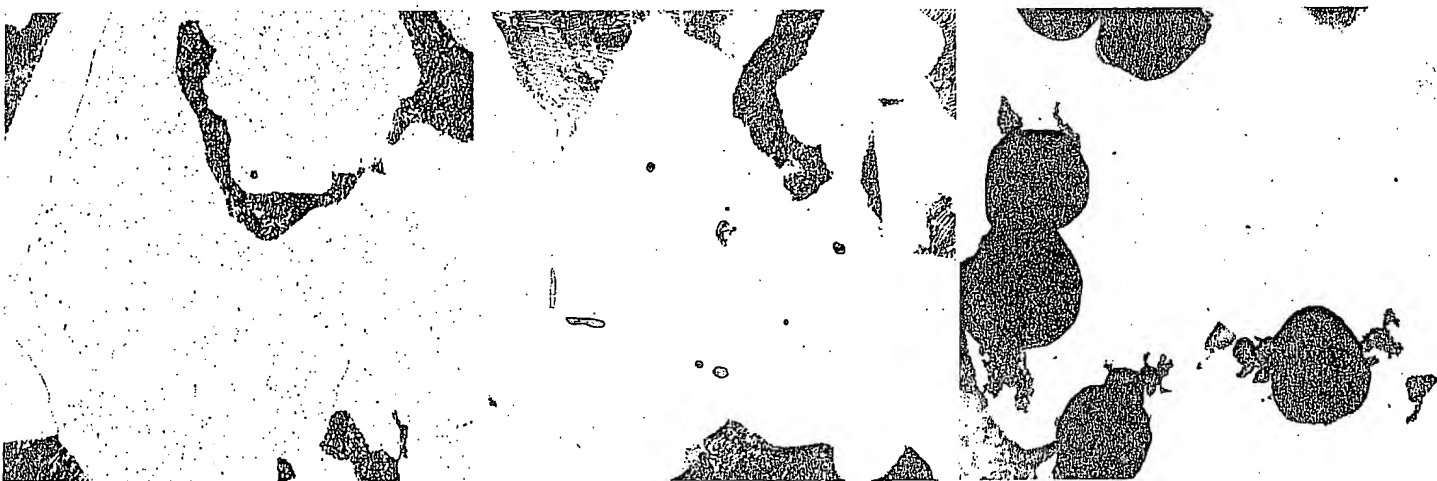
Nital   500×   Nital   500×   As polished (not etched)   500×

2882, 2883, 2884 Effect of type of suspending liquid used in vibratory polishing of low-carbon steel. Specimens were rough polished on 1-micron diamond and finish polished for 4 hr on 0.1-micron alumina. **Micrograph 2882 (left):** using propylene glycol; scratches have not been removed. **Micrograph 2883 (center):** using a mixture of two parts propylene glycol, one part water; results are satisfactory. **Micrograph 2884 (right):** using water; large corrosion pits have developed.
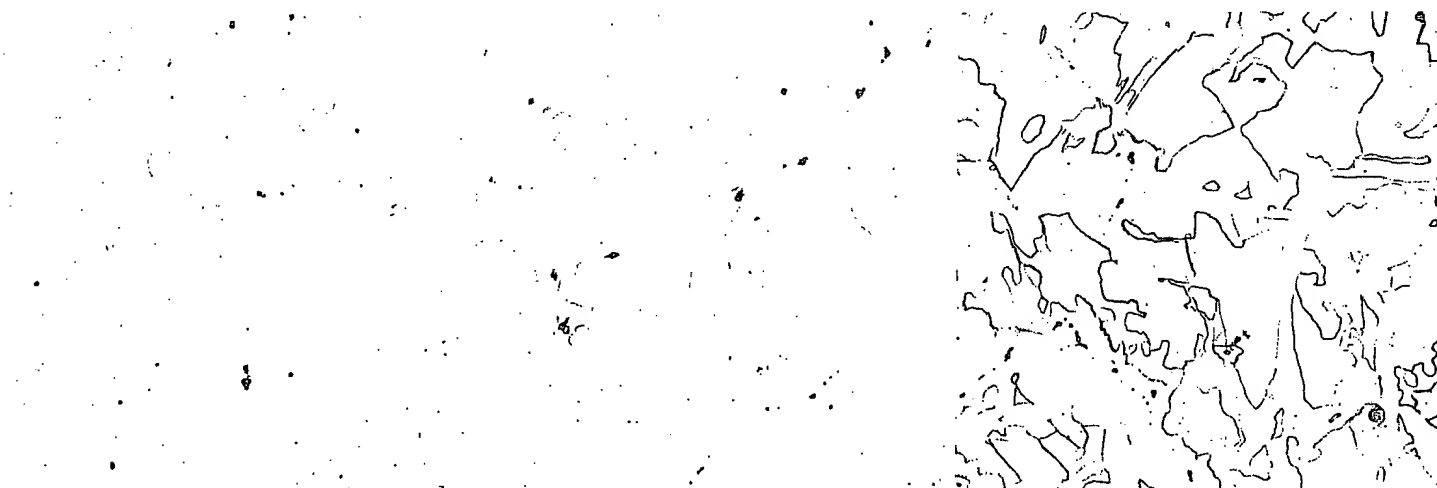
As polished (not etched)   100×   As polished (not etched)   100×   As polished (not etched)   100×

2885, 2886, 2887 Effect of load applied to the specimen in vibratory polishing of low-carbon steel. Specimens were rough polished on 1-micron diamond and finish polished for 4 hr on 0.1-micron alumina suspended in a mixture of 2 parts propylene glycol, 1 part water. **Micrograph 2885 (left):** using a 40-gram load. **Micrograph 2886 (center):** using a 70-gram load. **Micrograph 2887 (right):** using a 380-gram load. Etch relief develops during polishing, being greater the larger the applied load.

As polished (etched during polishing)   500×   As polished (etched during polishing)   500×   As polished (etched during polishing)   500×

2888, 2889, 2890 Effect of addition of different amounts of ammonium hydroxide to the suspending liquid in vibratory polishing of a cast alpha-beta brass. Specimens were polished with magnesia suspended in a mixture of three parts propylene glycol, one part water. **Micrograph 2888 (left):** using no addition of ammonium hydroxide; note numerous polishing scratches. **Micrograph 2889 (center):** using an optimum addition of ammonium hydroxide. **Micrograph 2890 (right):** using an excessive addition of ammonium hydroxide; note excessive relief between the two phases.
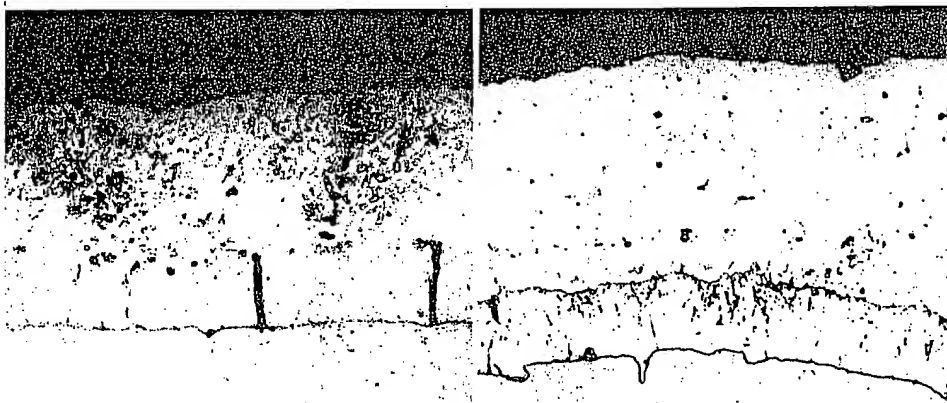
As polished (not etched)   700×   As polished (not etched)   700×

2891, 2892 Effect of pH of suspending liquid in the final polishing of specimens of galvanized iron. **Micrograph 2891 (left):** using a good-quality tap water. **Micrograph 2892 (right):** using a buffer solution with a pH of 7. The severe etching of the coating in micrograph 2891 occurred as the result of electrochemical differences between the zinc coating and the steel base.

Sometimes it is necessary to add a more aggressive etching reagent to the suspending liquid to ensure an adequate chemical component in the polishing mechanism. For example, the mechanism for an alpha-beta brass that was polished with the use of a straight glycol-water mixture had an excessive mechanical component, and final-polishing scratches became apparent as a result (micrograph 2888). The addition of a large amount of ammonium hydroxide caused the chemical mechanism to become predominant, and an unacceptable degree of relief developed between the two phases of the microstructure (micrograph 2890). Adjustment of the ammonium hydroxide addition balanced the two mechanisms to give an acceptable result (micrograph 2889).

The optimum polishing conditions have to be arrived at largely by empirical trials, guided by a few broad principles. However, highly reproducible results are achieved once the optimum conditions have been determined.

Electrochemical Differences. A further example of chemical effects arising during mechanical polishing is found in specimens containing constituents that differ considerably in their electrochemical characteristics. In galvanized steels, marked electrochemical effects arise between the zinc of the coating and the steel base metal. Severe etching of the coating occurs when a section is polished using water, even distilled water, as the suspending liquid, as shown in micrograph 2891. The effect can be eliminated by using a suspending liquid that has a pH very close to 7.0, thus suppressing electrochemical effects. This pH can be achieved with the use of a standard buffer solution; results are shown in micrograph 2892.

Edge Retention. Techniques used for edge retention are described under "Edge preservation" on page 3 in the article on Metallographic Methods. It is the purpose of the present discussion

only one that resulted in full grain-etching contrast, which is characteristic of a damage-free surface.

Vibratory Polishing. Vibratory methods are attractive for final polishing because they operate automatically and because they permit accurate control of polishing conditions. Results are highly reproducible once the controlling variables have been identified and optimized. A further advantage of vibratory polishing is that it can be adapted to chemical-mechanical polishing. The important variables in vibratory polishing are the abrasive, the nature of the liquid in which the abrasive is suspended, and the load applied to the specimen.

The effects of varying the suspending liquid are illustrated in micrographs 2882, 2883 and 2884. The polishing rate with straight glycol as the suspending liquid was so low that scratch traces from the previous polishing stage were still retained even after a protracted polishing time (micrograph 2882). Water as the suspending liquid provided fast polishing but developed severe etch pitting (micrograph 2884). A suitable mixture of the two provided an adequate polishing rate and a satisfactory polish (micrograph 2883).

Some etch attack occurs with the glycol-water suspending liquid, even with optimum adjustment of the liquid; the etching varies directly with the load applied to the specimen, as shown in micrographs 2885, 2886 and 2887. These three micrographs offer evidence that the polishing process is occurring by a chemical-mechanical mechanism, with the water acting as the active ingredient and the glycol (a chelating agent) acting as a modifier.

Nital   500×   Nital   500×   Nital   500×

2893, 2894, 2895 Effect of type of mounting plastic on edge retention of steel specimens polished by standard technique. Micrograph 2893 (left): specimen mounted in a phenolic plastic; also representative of edge retention using an epoxy. Micrograph 2894 (center): specimen mounted in an allyl plastic. Micrograph 2895 (right): specimen mounted in a polyvinyl formal plastic; also representative of edge retention using polyvinyl chloride plastic.

Nital   500×   Nital   500×   Nital   500×

2896, 2897, 2898 Effect of special techniques for improving edge retention of steel specimens mounted in an epoxy resin. Micrograph 2896 (left): steel shot incorporated in the mount; specimen finish polished by a standard technique. Micrograph 2897 (center): edge protected by an electrodeposited coating of nickel; specimen finish polished by a standard technique. Micrograph 2898 (right): specimen finish polished using a fairly rigid napless pad and diamond abrasive.

to relate edge retention to specific micrographs and the materials employed in their preparation.

With few exceptions, the abrasion rates of the plastics in which metallographic specimens are mounted are much greater than those of metals. The plastic abrades to a lower general level than the metal, and rounding of the specimen edge occurs to adjust for differences in level. The degree of edge rounding may be increased or decreased during polishing; long-nap polishing cloths increase edge rounding.

However, the abrasion rates of different types of plastics differ significantly, and edge retention can be improved by choosing a mounting plastic that has an abrasion rate matching as closely as possible that of the specimen. For example, progressively improved edge retention is obtained, as shown in micrographs 2893, 2894 and 2895, with the change from a phenolic (micrograph 2893) to an allyl (micrograph 2894) to a polyvinyl formal (micrograph 2895) mounting plastic. The matching of the abrasion rates of specimen and mount is important. Metals such as chromium and tungsten, which have very low abrasion rates, show poorer edge retention than that illustrated in micrograph 2895 even when mounted in a polyvinyl formal plastic. Metals such as copper and aluminum, which have high abrasion rates,

show good edge retention even when mounted in phenolic or epoxy plastics.

Reducing the difference in abrasion rate between the specimen and mount will improve edge retention. This may be accomplished by incorporating chips or pellets of a metal similar to the specimen in the mount face (see micrograph 2896). Any included material that reduces the abrasion rate of the plastic will also be effective. Another effective method for improving edge retention is to coat the specimen with a heavy electrodeposited layer of nickel (see micrograph 2897).

The napped cloths used in standard polishing procedures are likely to worsen the edge rounding developed during
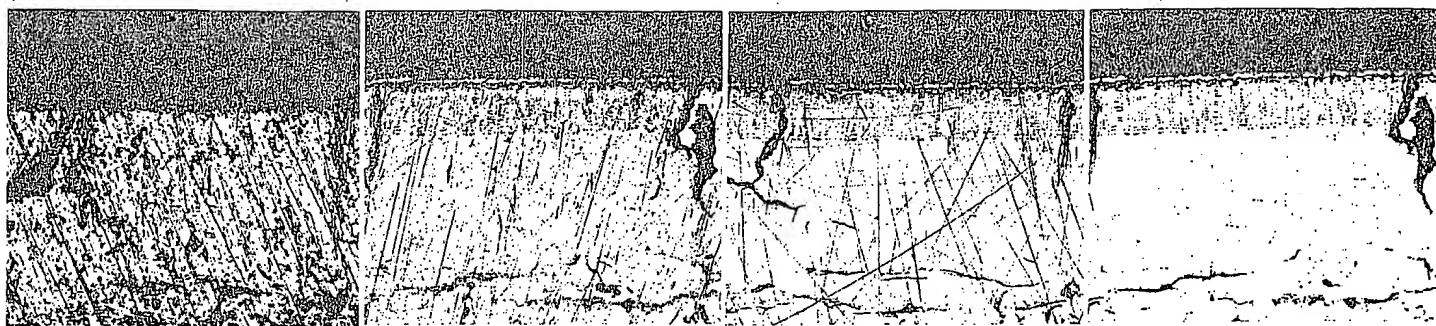
As polished (not etched)   70×   As polished (not etched)   70×   As polished (not etched)   70×   As polished (not etched)   70×

2899, 2900, 2901, 2902 Effect of different abrading and polishing techniques on the appearance of oxide scale on high-purity iron. **Micrograph 2899 (left):** specimen abraded on 400-grit silicon carbide paper; numerous chipping artifacts are present in the oxide. **Micrograph 2900 (left-center):** specimen abraded on a fine fixed-abrasive lap; minor chipping artifacts are present in the oxide. **Micrograph 2901 (right-center):** specimen abraded on a leadfoil lap coated with 1-micron diamond paste; oxide and metal are free from chipping artifacts, but they are badly scratched. **Micrograph 2902 (right):** specimen polished on 1-micron diamond abrasive on a cotton drill cloth after being abraded as described for micrograph 2901; oxide is free from chipping artifacts, and the surface of the specimen has an adequately scratch-free finish.

abrasion, because these soft cloths tend to conform locally to the contour of the abraded surface. If polishing is done on a fairly rigid pad so that contact is made during polishing only with high spots on the abraded surface, the specimen surface can be polished down to the level of the plastic. Hence, edge retention will be improved. Results obtained by this procedure are shown in micrograph 2898. When polishing on a rigid pad, careful selection of the polishing abrasive and cloth is necessary to avoid the development of excessive polishing scratches.

Surface Oxide Layers. Determination of the structure of a surface layer of oxide, or scale, on a specimen is sometimes the principal reason for metallographic examination. A specimen with such a surface layer presents a problem in edge retention. The oxide is usually friable, and thus susceptible to chipping and cracking during preparation. Because the detection of porosity or cracking in the layer is an important feature of the examination, it is essential to avoid the development of preparation artifacts that might be mistaken for such features. The develop-

ment of such artifacts during abrasion is likely, because treatment on standard abrasive papers often results in extensive chipping of the oxide layer (see micrograph 2899). Even a fixed-abrasive lap produces some artifact chipping (see micrograph 2900), but a special diamond-abrasive leadfoil lap produces a satisfactorily artifact-free result (see micrograph 2901). Then polishing with diamond abrasive on a hard napless cloth ensures that a high degree of surface flatness will be maintained and that no polishing damage will be introduced (see micrograph 2902).

Electrolytic Polishing

ELECTROLYTIC POLISHING, which is also called electropolishing, is most useful in the metallography of stainless steels, copper alloys, aluminum alloys, magnesium, zirconium and other metals that are difficult to polish by conventional mechanical methods. The electrolytic technique can completely remove all traces of worked metal remaining from the cutting, grinding and mechanical polishing operations used in preparing specimens.

When electropolishing is used in metallography, it is usually preceded by at least preliminary mechanical polishing and followed by etching.

Mechanism

Although the mechanism of electropolishing is not understood in all its aspects, the process is generally considered to include both a leveling (or smoothing) action and a brightening action. The nature of these phenomena is discussed below.

Smoothing. According to a theory developed by P. A. Jacquet in 1936, smoothing is accomplished by preferential solution of the "hills" or ridges on a rough surface, such as those that result from mechanical finishing. When such a rough surface is made the anode of a suitable electrolytic cell, a viscous liquid layer immediately adjacent to

this surface is produced by the reaction between metal and electrolyte. This layer of solution, known as the polishing film (Fig. 1), which has a greater electrical resistance than the remainder of the solution, controls the smoothing action.

The resistance at a peak A, represented by the distance A-B, will be lower than at depression C, represented by the distance C-D, because the film is thinner at A-B. The current at A will be much higher than at C, causing metal to dissolve faster at A than at C, and producing a nearly level, gently undulating surface by removing asperities a micron or more in size.

More rapid ionic and molecular diffusion through the thinner polishing film at A, as well as differences in anodic polarization phenomena at A and C, may also contribute to the leveling or smoothing action.
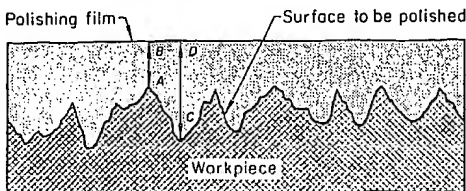
Brightening. The brightening action is related to the elimination of irregularities as small as about 0.01 micron and to the suppression of etching on the metal surface. This behavior is generally attributed to the formation of a thin, partly passivating film directly on the surface of the metal and following its contours.

Optimum brightening conditions have been related to local differences in anodic passivation at heterogeneities and between secondary peaks and crevices, along with the effects of passivation inhibitors that influence oxide-film formation and gas evolution. Similar factors may also contribute to the primary leveling or smoothing action in electropolishing (see P. V. Shchigolev, "Electrolytic and Chemical Polishing of Metals", Freund; Holon, Israel, 1970).

Current-voltage relations in electropolishing vary in different electrolytes and for different metals. The simple relation wherein polishing occurs over an extensive continuous range of currents and voltages is shown in Fig. 2. At low voltages, a film forms on the surface and little or no current passes; thus, etching occurs but not polishing. At higher voltages, polishing occurs. The perchloric acid electrolytes used for aluminum conform to this relation.

A more complex relation, frequently encountered, is shown by the curve in

Fig. 1. Mechanism of electrolytic polishing. See text for discussion.

CHEMICAL (ELECTROLESS) NICKEL PLATING

G.G.Gawrilov

PORTCULLIS PRESS

Chemical (Electroless) Nickel Plating

CHEMICAL (ELECTROLESS)
NICKEL-PLATING

by

G. G. GAWRILOV

PORTCULLIS PRESS
REDHILL

Contents

Ammonium hydrogen fluoride $(NH_4)HF_2$	15 g/l
Glycine $NH_2.CH_2COOH$	15 g/l
pH value (with NaOH)	8
Temperature	60-70°C
Speed of separation	10 μm/h

A. V. Ismailov and *S. B. Kalmikikov* [242] have protected the following composition for chemical nickel plating of magnesium alloys:

Nickel sulphate $NiSO_4.7H_2O$	20 g/l
Ammonium hypophosphite $NH_4H_2PO_2.H_2O$	30 g/l
Sodium pyrophosphate $Na_4P_2O_7.10H_2O$	50 g/l
pH value	9-10
Temperature	50-70°C

After chemical nickel plating, the components are subjected to heat treatment for 1 h at 150-200°C.

U.S. Patents 2916401, 1983634, 2993810, and 31221644 have also the separation of nickel-phosphorus alloys on magnesium surfaces as their subject.

13.7   Beryllium

In connection with the use of beryllium in nuclear technology and in aviation, methods for its surface improvement, among them also chemical nickel plating, were worked out.

R. M. Semenski, J. G. Beach and *R. E. Maringer* [243] on the one hand, and *K. Parker* and *H. Shah* [115] on the other, report about the coating of a beryllium mirror with nickel-phosphorus deposits, and they deal mainly with the internal stresses appearing in the coating. In [115] the conclusion was reached that one must use a solution with a concentration of hypophosphite of 0,4 Mol/l, pH value=4,0, and a separating temperature of 93°C under strict control of the separating conditions in *Kanigen* systems in order to obtain relatively "stress free" layers 100 μm thick on beryllium mirrors.

A research report by *W. H. Roberts* [244] was also published about the chemical nickel plating of beryllium components. The author asserts that the general working method of all the protected processes is approximately the following one:

(a) first cleaning; rinsing;
(b) second cleaning; rinsing;
(c) etching; rinsing;
(d) zincate treatment; rinsing;
(e) pickling;
(f) renewed zincate treatment; rinsing;
(g) nickel-plating 1st step;
(h) nickel-plating 2nd step; rinsing;
(i) heat treatment (optional).

The nickel solution should be used at 83 ± 1°C, and this temperature should be kept accurately as far as possible.

13.8   Titanium

Titanium is a metal which is similar to aluminium in its density, while it comes near to stainless steels with regard to its strength and its behaviour towards corrosion. In view of these favourable properties, titanium has found manifold uses in technology. Chemical nickel plating of titanium components is carried out for the purpose of improving some surface properties: increase in the resistance to abrasion, creation of prerequisites for soldering, improvement of appearance, etc.

The surface of titanium is always covered by an oxide film about 50 Å thick which prevents the adhesion of metal coatings. This oxide film is reproduced very soon

after its removal so that the applic
or hydride layers) is necessary to
The removal of the oxide film on
blasting, pickling, or by the use of
[245]
The intermediary layers of metal
The methods for their preparatio
and 13.5.2.
In order to obtain intermediary
pickled in a solution of the follov

     Nitric acid HNO_3 (D=
     Hydrogen fluoride HF (
     Temperature
     Duration of treatment

Afterwards, th: components are
     Acetic acid CH_3COOH
     Hydrogen fluoride HF
     Cathodes
     Current density
     Voltage
     Duration of treatment

For the formation of intermedia:
suitable mixtures of sulphuric a
In order to impart to titanium
nickel plating, *S. F. Yurev* and *I*
processing:
(a) sand-blasting;
(b) pickling in H_2SO_4 conc. at
(c) creation of an intermediary
     Ethylene glycol $C_2H_6($
     Hydrogen fluoride HF
     Zinc fluoride ZnF_2
     pH value
     Duration of treatment

Y. I. Valsyunene and *A. Yu. Pr*
ponents after degreasing and pi
     Nickel sulphate NiSO.
     Hydrochloric acid HC
     Ammonium fluoride I
     Duration of treatment

The intermediary contact layer
surface against oxidation. The
place in acid as well as possibl
phosphorus coatings on titan
measured 15 kp/mm² adhesion
intermediary hydride layer obt:
heat treatment at 400°C/1 h; :
20-26 kp/mm².

For chemical nickel-plating of
foremost on ceramics (for mic
recommended :[248]
     Alkaline electrolytic c
     Sodium hydroxide N

$_2$ 15 g/l

15 g/l

8

60-70°C

10 μm/h

tected the following composition

20 g/l

H_2O 30 g/l

50 g/l

9-10

50-70°C

subjected to heat treatment for

l644 have also the separation of

s their subject.

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(243) on the one hand, and K.

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haviour towards corrosion. In

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sistance to abrasion, creation

rance, etc.

e film about 50 Å thick which

film is reproduced very soon

after its removal so that the application of thin intermediary layers (metal, fluoride, or hydride layers) is necessary to obtain higher adhesion values.

The removal of the oxide film on the surface of titanium can be brought about by blasting, pickling, or by the use of both methods, one following the other.(220) (221) (245)

The intermediary layers of metal can consist of zinc, tin, copper, nickel, iron, etc. The methods for their preparation are similar to the methods described in 13.5.1 and 13.5.2.

In order to obtain intermediary layers of fluoride the titanium components are pickled in a solution of the following composition:

Nitric acid HNO_3 (D=1,4 g/ml)	250-300 g/l
Hydrogen fluoride HF (40%)	15-20 ml/l
Temperature	20°C
Duration of treatment	1-3 min

Afterwards, the components are worked anodically in the following solution:

Acetic acid CH_3COOH	875 ml
Hydrogen fluoride HF (40%)	125 ml
Cathodes	Stainless steel
Current density	2 A/dm^2
Voltage	2-3 V
Duration of treatment	5 min

For the formation of intermediary layers of hydride, the components are treated in suitable mixtures of sulphuric and hydrochloric acids.

In order to impart to titanium surfaces sliding properties by means of chemical nickel plating, *S. F. Yurev* and *E. V. Sakharov* (246) propose the following steps of processing:

(a) sand-blasting;

(b) pickling in H_2SO_4 conc. at 80°C, 2 min;

(c) creation of an intermediary contact layer in the following solution:

Ethylene glycol $C_2H_6O_2$	800 ml
Hydrogen fluoride HF (40%)	200 ml
Zinc fluoride ZnF_2	100 g
pH value	1-2
Duration of treatment	1,5-2 min

Y. I. Valsyunene and *A. Yu. Prokoptchik* (247) propose treatment of titanium components after degreasing and pickling in the following activating solution:

|	
Nickel sulphate $NiSO_4.7H_2O$	220 g/l
Hydrochloric acid HCl (D=1,19 g/ml)	120 ml/l
Ammonium fluoride NH_4F	20-40 g/l
Duration of treatment	2-3 sec

The intermediary contact layer thus obtained is a reliable protection of the titanium surface against oxidation. The deposition of the nickel-phosphorus alloy can take place in acid as well as possibly also in alkaline solution. The adhesion of nickel-phosphorus coatings on titanium is increased after heat treatment. Thus they measured 15 kp/mm^2 adhesion and maximum hardness of coating by means of an intermediary hydride layer obtained by pickling in concentrated sulphuric acid and heat treatment at 400°C/1 h; after heat treatment at 650°C/1 h the adhesion was 20-26 kp/mm^2.

For chemical nickel-plating of thin titanium films on a second carrier substance, foremost on ceramics (for micro switches), treatment in the following solutions is recommended:(248)
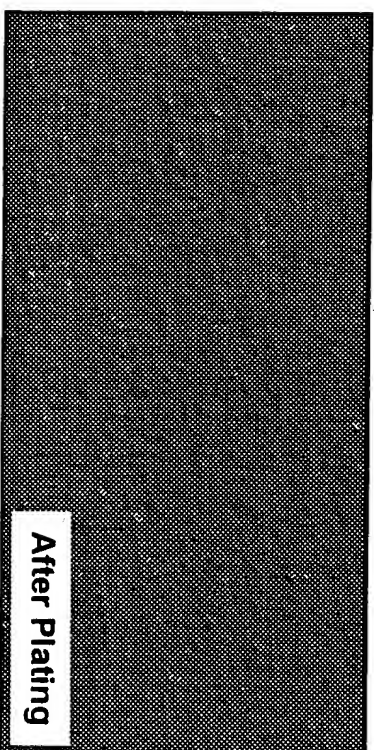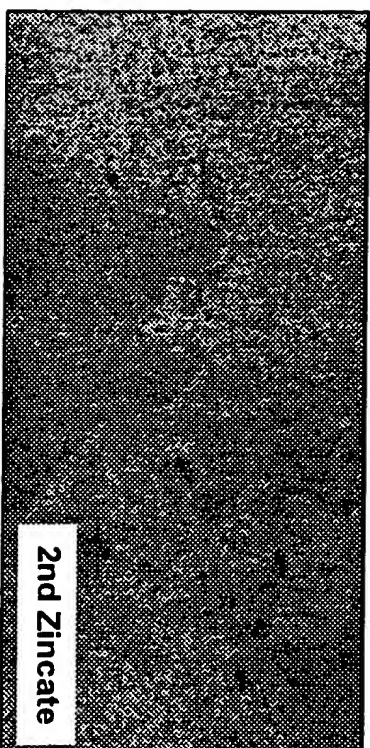
Alkaline electrolytic cleaning solution	
Sodium hydroxide NaOH	75 g/l

Plating on Superfinished Aluminum

Standard Process

2nd Zincate

After Plating

Advanced Process

2nd Zincate

After Plating

TILT 30°

16
May
2001
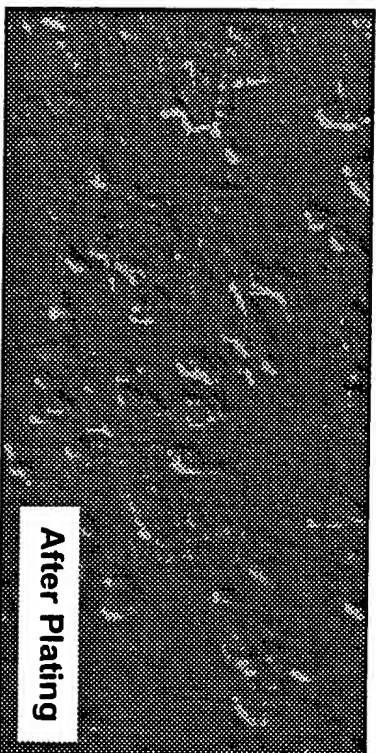
×1.5k 0106 10kV 20μm

FIDELITY DOLLY L #2

· LN3 GROUP I BEND TEST 1500X

88 Ni··12 P

5585

x1.5k 3000 12kV 20µm

x1.5k 0004 15kV 20µm

CONTROL BEND TEST 1500X